INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT

Addressing Methane at Anaerobic Bioremediation Sites

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Notice

IDEM Technology Evaluation Group (TEG) completed this evaluation of Addressing Methane at Anaerobic Bioremediation Sites based on review of items listed in the "References" section of this document. The IDEM OLQ technical memorandum *Submittal Guidance for Evaluation of Remediation Technologies* describes criteria for performing these evaluations.

This evaluation does not approve this technology nor does it verify its 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 found at some bioremediation sites may produce methane and methane concentrations of 5-15% (50,000-150,000ppm v/v) that are explosive, where 5% is the lower explosive limit (LEL), and 15% is the upper explosive limit (UEL). A site specific conceptual model should be developed, but in general methane concentrations in groundwater in excess of 10 mg/l or monitoring well/subsurface/ subslab gas concentrations in excess of 5,000 ppm v/v are a cause for concern. When methane concentrations are above 5,000 ppm v/v, monitoring is needed to determine if there is an adequate oxygenated vadose zone to mitigate the methane or if additional measures are necessary to protect any potential receptors. Note that 5,000 ppm v/v is 10% of the LEL (5% = 50,000 ppm).

Methanogenic conditions induced below a structure where oxygen is not as easily replenished present an added risk. Under these conditions a soil gas monitoring and a mitigation contingency plan should be proposed. Subslab gas concentrations exceeding 5,000 ppm v/v or 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.

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 not the chlorinated contaminants which are being bioremediated but rather the amendments used to establish 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, and 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.

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.

NOTE: Methane can also be generated without bioremediation treatment. While not described in this document, ethanol fuel releases (i.e. 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).

As summarized in Table 1, although excess amounts of soluble substrate amendments would be expected to produce methane at the greatest rate, some methane will be produced any time anaerobic conditions exist regardless of which substrate is used. If methane concentrations at anaerobic bioremediation sites are expected to reach 5,000 ppm v/v at identified receptors, a proactive methane monitoring plan should be initiated and a methane mitigation contingency plan outlined. Sites which would be expected to meet this criteria include sites with shallow groundwater where not enough oxygenated vadose zone thickness exists to dissipate methane, sites with preferential pathways (i.e. 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 is attenuating before reaching an area where it can accumulate. Either dissolved groundwater 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 conditions become 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).

<u>Screening Levels/Monitoring at Anaerobic Bioremediation Sites Table 1</u>

	Suggested Screening Levels and Actions for Soil Gas Methane at Anaerobic Bioremediation Sites		
Sampled Medium	**Concentration**	**Concentration**	**Action**
Groundwater	>10 mg/L	> 10 mg/l (same)	Monitor Soil Gas
Soil Gas External	>10% of LEL	> 5,000 ppm v/v	Check for receptors/ consider mitigation
Soil Gas Sub Slab	>10% of LEL	> 5,000 ppm v/v	Mitigate
	<10% of LEL	< 5,000 ppm v/v	Monitor
Indoor Air	>10% of LEL	> 5,000 ppm v/v	Evacuate/ Mitigate

<u>Groundwater</u>
Groundwater 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. As a worst case scenario, ground water methane usually will not accumulate to levels higher than the source concentration. The USGS recommends

that groundwater methane concentrations greater than 10 mg/l are an indication that methane concentrations may become a hazard (USGS, 2006). If groundwater concentrations exceed screening levels (10 mg/l), soil gas monitoring points should be placed in the direction of receptors and in any preferential pathways (e.g. 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 intrinsically safe Flame Ionization Detector (FID), combustible gas meter or collection of soil gas samples. 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 casing which may not be indicative of actual soil gas concentrations. Soil gas concentrations exceeding 5,000 ppm v/v 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 5,000 ppm v/v or 10% of the LEL indicate the need for mitigation. Responses less than 5,000 ppm v/v 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 5,000 ppm / 10% of the LEL, the mitigation plan should be implemented.

Indoor Air

Methane is flammable at concentrations between 5 and 15% of the LEL (50,000-150,000 ppm v/v). 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 5,000 ppm v/v or 10% of the LEL, indoor air concentrations should be measured. Indoor air concentrations greater than 5,000 ppm v/v or 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 5,000 ppm v/v or 10% of the LEL for methane.

Mitigation and Bioremediation Considerations:

The goal of mitigation is to eliminate the potential for 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 structural features.

If no 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 (i.e. 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 that could potentially produce methane would likely require a more active mitigation plan. During bioremediation, if microbially reducing conditions are created in soil under building floors, subslab depressurization or low flow ventilation should be incorporated into the remediation workplan to remove gases of concern from the subslab area (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 in soil under a structure; they will simply stop methane from entering the structure through the subslab. Only a properly screened collection system (such as SVE) will collect methane in soil beneath the subslab area.

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 Photoionization Detector (PID) will not measure methane. The higher 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.

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 5,000 ppm, 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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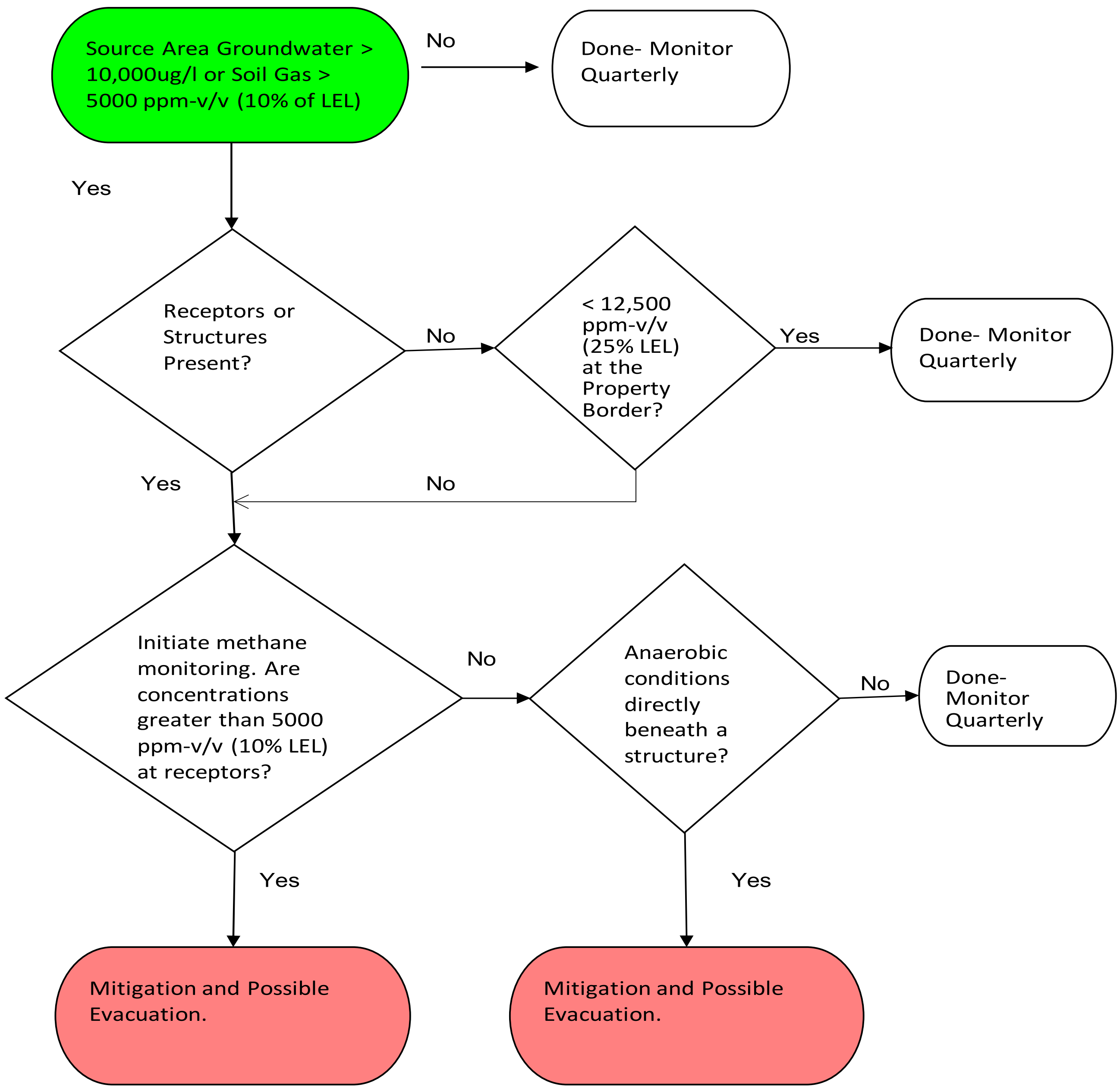
Suggested Process for Methane Monitoring at Anaerobic Bioremediation Sites



Appendix A – Percentages of the LEL Explained:

These concentrations and percentages are explained since percentages of a percentage are not typically used as a regulatory limit. 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%. 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.