

Remediation Division Methane Guidance

1.0 Introduction

This guidance provides general information about methane in the environment generated by landfills, dumps, feedlots, and contaminated sites, and general guidance on investigating, monitoring, and responding to methane at Minnesota Pollution Control Agency (MPCA) Remediation Division sites. **It is not intended to be a prescriptive document that covers all situations or scenarios, nor is it intended to replace program- or site-specific requirements.** Rather, this document supplements the related program-specific guidance listed below:

- [Best management practices for development on or near former dumps](#)
- [Vapor investigation and mitigation decision best management practices](#)
- [Vapor mitigation best management practices](#)
- [Investigation requirements at ethanol-blended fuel releases](#)
- [Vapor intrusion assessment performed at site investigations](#)

The process of methane investigation and characterization can be lengthy and often requires expedited response actions. Proactive communication with the MPCA project staff is expected. Regardless of the complexity of the site, regular communication with MPCA project staff is encouraged to ensure that all pertinent site issues and methane risk have been evaluated.

Where applicable, this document includes references to other Remediation Division program guidance for media-specific investigation, site decision, and remedy selection. Programs may use different terms to describe similar processes and actions, frequently based on applicable statutory language or historical usage. Terms used in this document were chosen for broadest applicability and understanding to describe general processes and actions. For example, the term “response action” was used to encompass corrective actions, cleanup actions, removal actions, mitigation actions, and remedial actions.

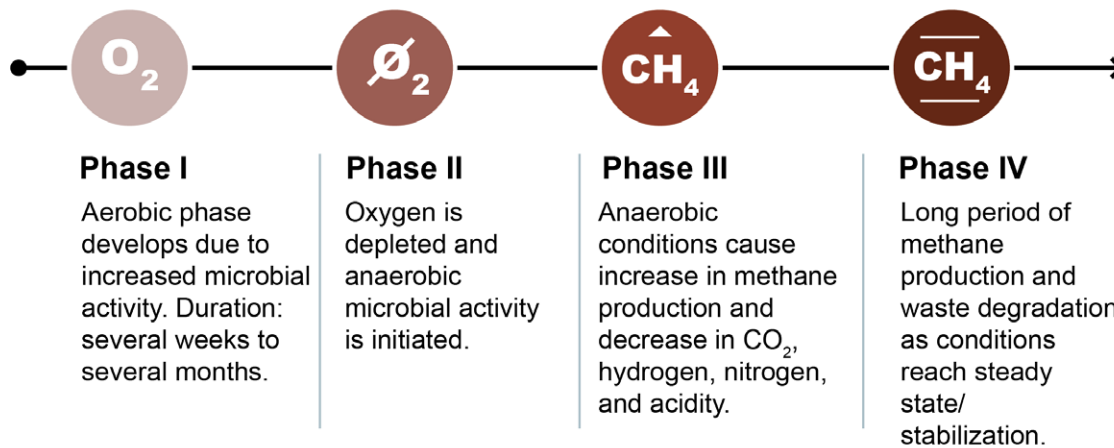
1.1 Methane in the environment

Methane

is a colorless, odorless, tasteless, flammable gas produced through microbial or thermal alteration of organic matter and is widely distributed in nature

Methane sources are well documented and include landfills and dumps, sewers, enhanced bioremediation (EBR) byproducts, petroleum hydrocarbon releases, feedlots, and natural sources such as wetlands, among others. Generally, methane is produced from degradation of organic matter under anaerobic subsurface conditions, and production can be delayed for days to years depending on the source and subsurface conditions. The dynamic properties of methane must be understood to evaluate risk.

Methane generation is generally divided into four distinct phases as outlined below.



The length of the four phases of methane generation will vary considerably for different settings depending upon the source, the composition of the material, moisture levels, temperature, physical setting, and operational practices on site. Methane can be generated in-situ over days to years and persist for decades based on the nature of the methane source and subsurface site conditions. This is further discussed in [Section 1.5](#).

Methane in landfills and dumps

Landfills and dumps are both waste disposal locations; however, landfills require permits to build, whereas dumps are unregulated solid waste disposal sites that never held a valid permit from the MPCA. Landfill gas (LFG) is generated through the decomposition of organic waste material and is composed primarily of methane and carbon dioxide. The large gas generation that occurs at landfills can result in pressure-driven flow into overlying or nearby buildings.

Methane production also varies between permitted landfills and unpermitted dumps. Methane concentrations at landfills and dumps are influenced by the *moisture content* (stormwater infiltration, snowmelt, contact with groundwater) and *type of waste* (inorganic waste produces less methane than organic waste).

A permitted landfill is constructed and filled using proper waste placement and compaction, and filling operations often account for specific waste types. Modern permitted landfills are capped with impermeable covers to limit the amount of moisture entering the waste. Unpermitted dumps may be constructed with insufficient compaction, a substandard cover, and comingled waste types. Additionally, unpermitted dumps may be constructed in floodplains or wetlands, which may increase methane production.

Methane in petroleum releases

Methane can be produced at petroleum hydrocarbon release sites due to anaerobic conditions. Ethanol-based fuel releases pose the greatest concern for methane generation due to ethanol's high oxygen content. Methane hazards can increase over time and reduce the oxygen available for biodegradation of aerobically degradable hydrocarbons. Methane generation may be delayed after a release and persist for years after the ethanol is no longer present in groundwater. The increased production of methane and carbon dioxide may strip petroleum hydrocarbons from groundwater and create a pressure gradient that facilitates undesired vapor migration.

At many petroleum release sites, the source area is small relative to other methane sources such as a landfill. Due to the smaller source area, petroleum release sites are not as prone to long distance methane migration. The Petroleum Remediation Program (PRP) follows program-specific guidance in responding to potential methane production at release sites. Refer to [Vapor Intrusion assessments performed during site investigations](#) for PRP handling of methane investigations at "standard" petroleum release sites. If initial site characterization under PRP guidance identifies methane at levels exceeding action levels in the source area (detailed in [Section 1.3](#)), additional response measures are warranted and should follow recommendations in this document.

Methane at bioremediation sites

Methane can be produced at bioremediation sites as a result of the remedy implementation establishing anaerobic conditions. Methane is generated through the consumption of organic carbon or electron donors. This fermentation creates byproducts such as carbon dioxide, methane, and water. Methane concentrations can change dramatically through the remediation process as anaerobic activity changes over time. Peak production periods can occur weeks to months after remedy implementation. Methane concentration variability should be considered during monitoring activities. Bioremediation may be accelerated through biostimulation (added nutrients) or bioaugmentation (added microorganisms), further increasing the rate of methane production.

Methane at historical feedlots

Methane at feedlots is generated by anaerobic digestion (biological oxidation without oxygen) of organic substances such as livestock waste and byproducts. Animal agriculture is responsible for the majority of methane emissions in Minnesota, specifically from manure management and cattle digestion. Historical feedlots have resulted in identified sources of methane due to the long-term operation and subsequent burial of animal waste and byproducts.

Naturally occurring methane

Methane production associated with naturally occurring buried organic deposits (e.g., peat) can be difficult to distinguish from anthropogenic methane sources; however, a variety of forensic methods are available for differentiating methane sources. Methane can be generated in soils (via methanogens) and methane also can be consumed in soils (via methanotrophs). All soils tend to be either producers or consumers of methane. Within a given soil column, methane may be produced at depths where the soils are anaerobic, and any vapors migrating upwards may be consumed within shallower soil layers where the soils are aerobic.

1.2 Methane risks/hazards

The principal health and safety concerns of elevated methane are related to the explosive and asphyxiant properties of gas-phase methane, which are considered acute hazards. Methane may also cause ecological impacts.

Explosive hazards

Methane gas presents an explosion and fire hazard. Methane can migrate laterally and vertically through the unsaturated soil column and collect in enclosed or confined spaces where a spark or other ignition source can trigger an explosion or fire. While soil gases may not be an explosive risk in-situ, methane creates hazards if a sufficient volume of gas migrates into an enclosed space, including, but not limited to, subgrade utilities, wells, and crawl spaces, causing oxygen to be displaced. As noted in [Section 1.1](#), methane can migrate variable distances.

Explosive conditions exist for a specific combustible gas between its Lower Explosive Limit (LEL) and its Upper Explosive Limit (UEL). The LEL for methane corresponds to 5 percent (%) methane by volume in air, which is equivalent to a relative concentration of 50,000 parts per million by volume (ppmv) methane. The UEL for methane is 15% methane by volume in air or 150,000 ppmv. This is further discussed in [Section 1.3](#) Regulatory Framework. It is important to exercise care when drilling into areas with potentially high methane concentrations. Ambient air and down-hole gas monitoring should be conducted at and around boreholes when drilling into areas with potentially high methane concentrations. Additionally, intrinsically safe remediation equipment must be used at any site where methane is likely to be present.

Asphyxiation hazard

Methane can displace oxygen, which can result in the potential for asphyxiation. The accumulation of such lethal levels is especially a concern in confined spaces, such as underground utility structures and trenches and within enclosed spaces in buildings located at or near the source area. Methane concentrations resulting in asphyxiation are higher than the explosive concentrations of methane. Asphyxiation occurs at 500,000 ppmv (50% methane in air), but the worker exposure limit is 1,000 ppmv (0.1 % methane in air) for an 8-hour shift due

to cumulative effects of methane in the blood from breathing concentrations above this level over an 8-hour shift.

Reversible symptoms of methane exposure include fatigue, dizziness, and headaches, and progress to more severe symptoms of nausea, agitation, and displaced speech. Other contaminants may also be present along with methane and pose chronic inhalation risk (e.g., other components of LFG and volatile organic compounds [VOCs]).

Ecological/Natural resource risks

Methane risk for ecological impact is asphyxiation, which can stress or kill plant life. Stressed vegetation may be indicative of methane gas migration asphyxiating the plant’s root system. Most plant root systems are relatively shallow and would only be affected by the presence of methane near the ground surface. The lack of stressed vegetation does not preclude the presence of methane at deeper intervals.

1.3 Regulations and policies

The MPCA has established action levels for groundwater, soil gas, and ambient air. If groundwater or gaseous methane concentrations are detected at a remediation site above the action levels, contact the MPCA Project Manager assigned to the site. Additional notifications may be warranted as outlined in [Table 1](#) and discussed in Emergency Response below. Notify the Minnesota Duty Officer at 651-649-5451 or 1-800-422-0798.

The MPCA does not provide oversight of response actions or issue liability assurances related to naturally occurring methane. However, levels of naturally occurring methane that exceed action levels should be treated as a potential health and safety concern and addressed to manage risk to building occupants.

Air and soil gas limits

Methane production at a remediation site may result from a combination of a release to the environment and natural sources, in which case the MPCA will require a response action if an MPCA action level is exceeded. Other regulatory agencies also manage methane. For example, the Occupational Safety and Health Administration (OSHA) sets a flammable gas action level (including methane) for confined spaces to protect workers in the workplace. In instances where methane concentrations exceed OSHA workplace standards, employers must comply with OSHA’s standards to ensure the safety of workers which may include monitoring, ventilation, and/or training. The MPCA action levels for methane in air and soil gas are outlined in [Table 1](#).

Table 1: MPCA action levels for existing building(s)

| | LEL action level (at or exceeding) | Methane % by volume action level (at or exceeding) | Response action |
|--------------------------|------------------------------------|--|--|
| Exterior soil gas | 10% of the LEL | 0.5% methane by volume (5,000 ppmv) | MPCA notification and building-specific exterior soil gas or sub-slab soil gas investigation |
| Sub-slab | 10% of the LEL | 0.5% methane by volume (5,000 ppmv) | MN Duty Officer notification and initiate control measures |
| Indoor air | 10% of the LEL | 0.5% methane by volume (5,000 ppmv) | Fire Department and MN Duty Officer notification, initiate control measures |
| Confined space* | 10% of the LEL | 0.5% methane by volume (5,000 ppmv) | Fire Department (911) notification; evacuation and/or entry prohibited |

*Confined space limits are set by OSHA as 10% of the LEL action level (OSHA 1915 Subpart B App A)

Refer to [Appendix B](#) for recommendations on accurate reporting of methane data and [Appendix C](#) for instructions on converting between percent methane, methane by volume (ppmv), and methane by percent of the LEL.

Groundwater limits

Groundwater sampling for methane is not required at many sites. There are certain instances where the MPCA recommends evaluation. Such sites include ethanol-blended fuel releases; sites with remediation systems (e.g., groundwater extraction and treatment systems) near certain sources; unlined landfills and dumps; or sites undergoing EBR with high organic content. The MPCA screening level for methane in groundwater is 10 milligrams per liter (mg/L). Groundwater (aqueous methane) concentrations exceeding 10 mg/L require MPCA notification and may require additional groundwater and/or soil gas monitoring. Specifically, the MPCA recommends additional monitoring for detections of aqueous methane between 10 to 28 mg/L and immediate action at aqueous methane detections at or exceeding 28 mg/L. Further discussion of the stepwise approach to methane investigation is discussed in [Section 2.0](#).

Emergency response

As noted in [Table 1](#), a concentration of methane at 10% of the LEL or greater in indoor air is cause for evacuation of a building **if** concentrations cannot be mitigated immediately. Usually, methane accumulates to such high levels in confined or enclosed spaces (see Confined Space in [Table 1](#)). The decision to evacuate a building should be made in consultation with the local fire department. Local fire departments may have their own protocol for building evacuation and for reentering a building following evacuation. At a minimum, a building or an enclosed space with methane concentrations at 10% of the LEL or greater should not be entered following evacuation, except by a person properly trained and wearing the proper personal protective equipment and authorized by the local fire department. Further methane response actions are detailed in [Section 4.0](#).

At 28 mg/L, the water is fully saturated with methane and there is an increased risk that air space in the well is at or approaching the LEL. For detections at or exceeding 28 mg/L, if groundwater is shallow and detections are in or near structures, immediately remove any potential ignition sources, evaluate indoor air and points of entry, and vent gas away from confined spaces. The air and out-gassing methane, not the water, is now flammable and potentially explosive and should be addressed following methane gas recommendations outlined herein.

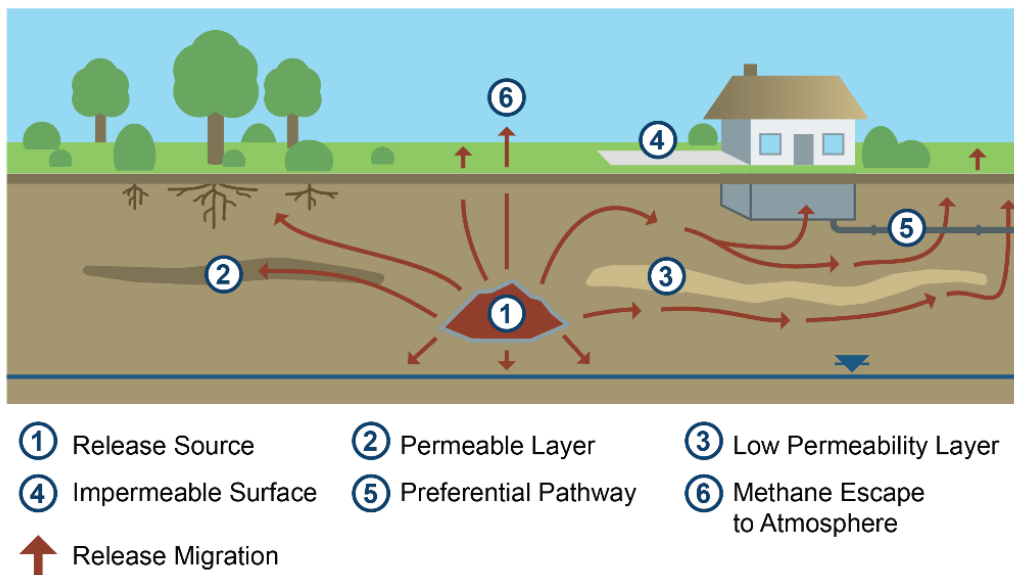
1.4 Conceptual site model

A conceptual site model (CSM) should be developed to evaluate the potential for methane generation and migration. A CSM is a description of the conditions and the physical, chemical, and biological processes that control the transport, migration, and potential impacts of contamination at a site. The CSM is discussed in greater detail in the [MERLA Remediation process and risk-based site evaluation guidance](#) and the [Petroleum soil and groundwater investigation guidance](#). Consider methane-specific attributes that may be critical in evaluating the methane risk such as confined spaces, anaerobic conditions, and subsurface pathways for methane migration.

1.5 Fate and transport

Understanding the source, life cycle, and movement of methane is key to designing a sampling plan that will accurately identify potential risk. The primary mechanisms for methane migration are diffusion and pressure-driven (advective) flow in response to subsurface and atmospheric pressure gradients as depicted on [Figure 1](#).

Figure 1: Generalized model of methane production and migration



Methane and other gases are expected to migrate laterally and vertically along preferential pathways where more permeable native soils, fill, or other porous substrate (e.g., karst systems) are present. Methane may be transported along anthropogenic pathways, such as utility corridors, which are backfilled with coarser aggregate than surrounding soils. Methane moves from high pressure (at depth or beneath a capped surface) to low pressure (towards ground surface and into the atmosphere).

Relative changes in barometric pressure may cause an increase in vertical and lateral methane migration in the subsurface. Temperature can influence methane production, altering the rate of microbial activity. Frost conditions during winter months can enhance lateral migration when vertical pathways are limited by frozen soil. Methane gas must be sampled or monitored to account for seasonal variability.

[Table 2](#) provides several factors which influence methane generation and migration.

Table 2: Gaseous methane migration influences

| General factor/Attribute | Increased migration potential | Decreased migration potential |
|--------------------------------------|---|---|
| Soil type | Permeable soil (sandy) | Less-permeable soils (silt or clay) |
| Soil moisture content | Dry, well-drained | Wet, high groundwater, wetland |
| Waste type | High organic content such as household garbage (municipal solid waste), demolition debris (wood), ethanol release | Low organic content such as non-degradable demolition debris (concrete, bituminous, metal), ash, petroleum releases limited in extent |
| Waste pile/Source depth | Deep trench | Shallow fill |
| Waste/Source volume or mass | > 500,000 cubic yards, large | < 500,000 cubic yards, small |
| Groundwater table (if source) | Shallow groundwater table | Deep groundwater table |
| Seasonal variation | Frozen soil prevents natural venting | Thawed soil can vent easier |
| Subsurface variation | Sand seams, utility trenches (and associated backfill) | Homogenous soil |
| Engineered surfaces | Pavement, buildings, landfill caps | Undeveloped land/greenspace |

2.0 Methane investigation

The MPCA takes a stepwise approach to methane investigation and characterization. Methane production is variable over time and may migrate, altering the contaminant plume boundary. Methane may be the primary contaminant of concern and the risk driver for corrective action or long-term monitoring at a site. In many instances, non-methane contaminants such as VOCs associated with historical releases (e.g., trichloroethylene, benzene, etc.) may also be present in soil gas and must be evaluated in addition to methane hazards.

Sampling and monitoring are expected to be conducted by trained personnel. Prepare a site-specific sampling plan for MPCA review and approval. A sampling plan should reference or include specific information regarding quality assurance/quality control (QA/QC) measures required for the project. Refer to [Appendix E](#) for information regarding QA/QC measures.

2.1 Receptor survey

The MPCA recommends conducting a receptor survey prior to the site investigation to identify potential high-risk receptors and optimize site work. A receptor survey for a methane investigation should include water supply well and/or vapor receptor surveys. Evaluate preferential pathways and potential points of gas entry for potential sparking prior to conducting gas monitoring. Examples of features to consider during the survey include the following:

- Sewers and vents
- Floor sumps, elevator shafts, dry wells, vaults
- Electrical conduits
- Foundation, foundation cracks, unsealed earthen floors, utility penetrations, engineered caps
- Occupied enclosures, confined spaces, and crawl spaces

When conducting a building vapor survey for potential emergency conditions:

Check buildings and basements that the vapor risk assessment indicates may be impacted using both an explosimeter and 4-gas meter to take vapor readings. Record names, addresses, and telephone numbers of building owners/occupants. Refer to [Appendix D](#) for discussion of field meters.

Take methane readings to assess explosive conditions in the basement, near sewer drains, cracks in the foundation, at covered sumps, building corners, crawl space, or in any area of poor air circulation.

2.2 Vapor intrusion

Gaseous methane sampling is required at sites where methane production is suspected or known. Methane evaluation requires a different set of considerations than typical vapor intrusion sites due to the fundamental differences between VOCs and methane. Due to the acute risks and potential emergency response conditions associated with methane, when the presence of methane has been established onsite, it becomes the primary concern. Location of potential receptors, preferential pathways for methane migration, gas pressures, and relative concentrations of methane and oxygen are important considerations during a methane gas investigation.

Program-specific vapor guidance and recommendations should be used as a reference when designing a vapor investigation.

Site conditions must be recorded during methane investigation, including the following:

- Temperature
- Barometric pressure
- Indications of stressed vegetation in localized areas

Many methane investigations begin with sampling exterior soil gas and expand to sub-slab and indoor air evaluation based on analytical results and established risk. However, if there is a receptor at obvious potential risk due to anticipated high concentrations of methane and/or proximity to the source, an investigation for methane within the building should be conducted first.

Based on preliminary results, additional site characterization and/or routine monitoring may be recommended and will require updates to the MPCA-approved site-specific sampling protocol. Refer to [Section 3.0](#) for further discussion on site decisions.

2.2.1 Soil gas

Conduct a soil gas investigation at a site with a methane gas concern to assess concentrations, migration, and risk levels to nearby or proposed structures. Temporary soil gas probes can be used to monitor methane at various sites. Correct probe installation will ensure the sample is collected from the appropriate target depth and prevent surface air interference. Soil gas probe sampling and monitoring data will typically be the most useful indicator of methane gas migration and can be used to establish a methane gas area of concern. Based on the action levels described in [Section 1.3](#), the area of concern is defined by methane concentrations at or exceeding 10% of the LEL. The soil gas investigation may eliminate the need to expand monitoring activities to a nearby building.

Sample locations

Locate soil gas samples to evaluate the source area and delineate the extent and magnitude of methane gas in all directions. The location and number of soil gas sample locations will depend on site-specific conditions. Specific attention should be paid to determining if methane is migrating towards buildings at concentrations of concern by sampling between source and surrounding receptors within the site or property boundaries, as applicable.

Sampling should also be conducted along preferential pathways such as subsurface utility lines or trenches. Carefully identify and accurately locate utility corridors on a site map. Authorities responsible for maintaining

these utilities must be notified because the interior atmosphere of manholes, and other utility confined spaces, will require monitoring prior to access. Field technicians performing the sampling must be properly trained and certified based on the characteristics of the environment being assessed (e.g., confined space). Additional gas monitoring may be required in manholes or within the soil gas near or adjacent to a structure to evaluate the potential for temporal and seasonal fluctuations within the soil gas.

2.2.2 Sub-slab soil gas

Conduct sub-slab soil gas sampling in accordance with the MPCA's [Vapor investigation and mitigation decision best management practices](#) beneath structures where a risk of methane migration has been identified during the initial soil gas assessment (e.g., if methane concentrations in soil gas near a building equal or exceed 10% of the LEL) or when a receptor-specific sample exhibits a methane concentration above the action level. Conduct a vapor intrusion building survey to determine potential entry points for methane intrusion and to identify potential enclosed spaces where methane might accumulate.

If sub-slab concentrations beneath a structure or in preferential pathways equal or exceed 10% of the LEL (5,000 ppmv), indoor air concentrations must be analyzed, and active response measures are warranted.

Sampling locations

Sub-slab sample locations should be selected and installed in accordance with the MPCA's [Vapor investigation and mitigation decision best management practices](#) and the number of samples should adhere to the recommended number of sub-slab samples based on building size as detailed in [Appendix C](#) of that vapor Best Management Practices document. Deviations from the recommended sample amount must be approved by the MPCA Project Manager.

2.2.3 Indoor air

If the potential for methane gas migration into a building has been identified, evaluation of the building is a high priority. Depending on the site, methane gas monitoring within buildings may be an integral part of the investigative phase, an interim measure until gas controls are installed, or part of a long-term monitoring program to ensure methane is not entering buildings.

Sample locations

Sampling of indoor air should include worst-case locations where methane might accumulate and specific point of entry locations. Before indoor air sampling is conducted, complete the building vapor survey to identify confined or enclosed spaces and potential points for gas entry into the building.

Monitor specific locations identified as having vapor concerns in at least two locations: low, near the floor or near the possible gas entry location, and high, along basement ceiling rafters or ceiling corners where methane gas, which is lighter than air, may have risen and become trapped.

2.2.4 Sample methods and frequency

The MPCA recommends soil gas, sub-slab, and indoor air samples be collected in accordance with the MPCA's [Vapor investigation and mitigation decision best management practices](#). At a minimum, samples should be collected within the MPCA-defined heating season (November 1 through March 31) and non-heating season (April 1 through October 31) to account for seasonal variability. Methane generation is variable over time; therefore, confer with the MPCA Project Manager regarding additional sampling or monitoring required based on site-specific conditions. Seasonal sampling is required unless detections exceed 10% of the LEL, in which case proceed with immediate response actions or additional sampling as outlined in [Section 3.0](#) and [Appendix A](#).

Collect samples using evacuated canisters and submit for laboratory analysis to characterize vapors at the site. During sampling, use a field monitor to record gas composition (percent methane, percent carbon dioxide, and percent oxygen by volume) at each sampling location (refer to [Appendix D](#) for recommended equipment); also record the percent LEL. If this is not indicated by field measurements, it can be calculated using the information in [Appendix C](#). In addition, for soil gas and sub-slab samples, pressure readings should be collected using a field

meter (as specified in [Appendix D](#)) at each sampling point during each sampling event. Field meters can also be used if the results are time critical, for example, to assess any emergency response conditions within the building.

Additional indoor air monitoring locations and frequency are dependent on the previous measurements recorded, locations where high methane concentrations have been detected in exterior or sub-slab soil gas, or where elevated levels of methane have been detected at potential gas entry points. Field measurement detections of indoor air should be considered under the lens of the emergency response measures outlined in [Section 2.1](#) and the MPCA decision matrix outlined in [Section 3.0](#) and [Appendix A](#).

Landfill sites have specific minimum sampling requirements. If a site-specific plan exists for the landfill, then the sampling shall be conducted according to that plan. Additional sampling events may be required outside of the site-specific plan based on analytical results and as determined by the MPCA Project Manager. If no plan exists for the individual landfill, all sample locations at the landfill shall be sampled at the same time as the monitoring wells.

2.2.5 Analytical methods

Laboratory analysis provides more accurate results than use of portable gas meters, especially for lower concentrations. Samples should be submitted to a Minnesota-certified laboratory for analysis. When samples are collected for laboratory analysis, use one of the following analytical methods:

- United States Environmental Protection Agency (EPA) Test Method TO-3
- ASTM International (ASTM) Method D1946
- EPA Test Method 3C

The MPCA recommends methane analysis by EPA Method TO-3 for fixed gases (methane, oxygen, and carbon dioxide) unless directed otherwise by the MPCA Project Manager.

Choose a laboratory analytical method that will result in a reporting limit that is below the action level and can provide meaningful data. A single 1-liter (L) or 6L canister will supply enough sample volume to complete the EPA Method TO-15 and fixed gas/methane analyses. Depending on the laboratory utilized, the reporting limit may change based on the sample canister volume (1L versus 6L canister). Laboratory QA/QC requirements for EPA Method TO-15 and fixed gases should be considered prior to sampling. It is imperative to confirm reporting limits (RLs) and method detection limits (MDLs) with the laboratory when determining the appropriate analysis. Refer to [Appendix D](#) for discussion on the laboratory analytical methods.

2.3 Groundwater

Groundwater sampling for methane is not required at all sites where gaseous methane is a concern. Groundwater sampling is recommended based on site-specific conditions; for example, ethanol-blended fuel release sites, sites with groundwater remediation systems near certain sources, unlined landfills or dumps, or sites undergoing EBR with high organic content. Collect methane samples first within the suite of analytes to avoid volatilization losses to ensure meaningful comparison to the 10 mg/L action level. Refer to the [MERLA groundwater investigation guidance](#) and the [Petroleum soil and groundwater investigation guidance](#) for general information on conducting a groundwater investigation. Refer to [Investigation requirements for ethanol-blended fuel releases](#) for information specific to ethanol-blended fuel release groundwater investigations. Record well installation and sampling methods to interpret analytical results. Groundwater evaluations typically take a stepwise approach from initial site characterization through investigation to determine extent and magnitude. If methane is detected in groundwater samples exceeding 10 mg/L, additional plume delineation and subsequent soil gas sampling may be required to determine if additional receptors are being impacted.

2.3.1 Monitoring frequency and location

Assess groundwater impacts by installing permanent monitoring wells to define groundwater flow conditions and investigate water quality upgradient and downgradient from the source. Because methane can be generated in-situ over time, long-term monitoring may be needed to characterize the release and assess risk. The MPCA strongly recommends installation of permanent monitoring wells, rather than grab sampling from temporary wells. The location and number of monitoring wells required will depend on site-specific conditions; however, a general guideline is outlined below:

- One or more wells near the source of the release.
- One or more wells along the longitudinal axis of the contaminant plume.
- One background well upgradient from the source of the release.
- One or more wells along the outer boundary of the contaminant plume.

Therefore, a minimum of three monitoring wells must be installed outside the source area, one upgradient and two downgradient. Additional wells may be required based on the location of receptors or preferential pathways relative to the release. If a methane plume is identified moving towards an existing building, further building-specific soil gas points or sub-slab sampling may be required to determine risk to building occupants.

For sites undergoing EBR, wells should be installed near or in the area undergoing EBR treatment, and between the EBR treatment areas and potential receptors.

Monitoring wells with long well screens tend to draw water from over a larger area and may result in diluted samples. Size monitoring well screens appropriately to the zone targeted for monitoring. Screens should typically be set below the water table a short distance to minimize potential degassing. Following review of water table elevation, additional monitoring wells with shorter well screens or multi-level wells may be required.

3.0 Site decision

Site decisions are made based on determining whether unacceptable risk exists at a site. Methane investigation focuses on a worst-case, acute condition for an existing building, whereas a VOC-related soil vapor investigation evaluates acute, sub-chronic, and/or chronic exposure and associated risk.

The risk is dependent on the detected concentrations, the potential for gas accumulation, the number and type of receptors in the immediate area, proximity to an ignition source, and response time required to seal and eliminate gas points of entry. Acute conditions may warrant emergency response if methane concentrations exceed any of the limits in [Table 1](#). Site decisions may include conducting additional investigation and/or completing a response action as outlined in [Section 4.0](#).

Once the presence of methane has been established, continued investigation and/or response actions are required following guidance in this document, as well as program-specific guidance ([MERLA Remediation process and risk-based site evaluation guidance](#), [Petroleum risk evaluation and site management decision guidance](#), and [Investigation requirements for ethanol-blended fuel releases](#)). Sites may require referrals for continued investigation, to delineate the full extent and magnitude, and to implement additional response actions. For example, a site beginning in the Voluntary Investigation and Cleanup program may be referred to Site Assessment for further characterization. Communicate with the MPCA Project Manager for the site when planning the objectives and scope of the investigation. Reference should also be made to the existing guidance for specific sources (i.e., landfill, petroleum, and Brownfield sites) identified in [Section 5.0](#).

3.1 Risk evaluation and additional investigation

The MPCA uses a risk-based framework in determining site decisions and response actions for methane detections at a site. Additional investigation may be necessary when the extent and magnitude of contamination has not been defined. While an initial site investigation may not require all media be evaluated, subsequent data will inform the scope of the additional investigation. The MPCA expects routine communication as the scope of

an investigation and response actions evolve. Below is a generalized process for evaluating the level of site characterization and response actions warranted for groundwater, soil gas, sub-slab soil gas, and indoor air. Consult the MPCA Project Manager for approval before undertaking investigation or response measures that are less conservative than those outlined in the recommended response actions outlined below.

Vapor intrusion

When assessing gaseous methane, identify the source of methane for any detections. If the source is the result of a utility leak, contact the utility company. The local fire department may be able to assist in evaluating source for indoor air or points of entry detections. If the source is environmental, utilize the MPCA's recommended risk-based response action approach outlined in [Appendix A](#). Response actions begin with completing the remaining seasonal sampling and progress to implementing control measures to long-term monitoring based on the detections of methane. When detections meet or exceed the Action Levels outlined in [Table 1](#), control measures are warranted. MPCA, MN Duty Officer, and/or local fire department notification will be required based on the detections as outlined in [Table 1](#) and [Appendix A](#). A summary of the stepwise response actions to methane detections is outlined below.

Soil gas

For detections in soil gas below 10% of the LEL in appropriately located and constructed soil gas probes in two seasons, the methane gas area of concern associated with the source (landfill, dump, ethanol release, etc.) has been defined. If methane is detected in the outermost gas probes at concentrations equal to or greater than 10% of the LEL, the methane gas area of concern has not yet been defined, and additional investigation is required. Options include collecting additional, building-specific exterior soil gas samples or collecting sub-slab samples. Control measures, including ventilation wells and eliminating spark sources, are required for soil gas detections equal to or greater than 25% of the LEL. At detections above 50% of the LEL, expedited control measures are required.

For a large and significant methane source, several years of soil gas data may be necessary to fully understand long-term risk from methane, due to the many factors that can influence the generation and movement of methane gas. At a landfill site, the soil gas data collected to-date are not necessarily representative of long-term conditions. Given the documented presence of a continual LFG source and potentially unstable/changing conditions associated with the LFG plume, an active sub-slab soil gas mitigation system may be warranted and required for an on-site building to appropriately manage long-term vapor intrusion risk.

Sub-slab soil gas

Sub-slab sampling may occur as part of the initial site investigation or in response to detections of methane in soil gas. For detections of sub-slab methane below 10% of the LEL in two seasons, no further pathway evaluation is required. Sub-slab detections equal to or greater than 10% of the LEL require further investigation in indoor air and points of entry and active building mitigation. Post-mitigation diagnostic sampling and testing is required following mitigation. Refer to [Section 4.0](#) for further discussion on active building mitigation.

Indoor air

Initial indoor air monitoring will be more frequent in buildings where explosive gases were detected as outlined above. For detections of methane in indoor air, eliminate obvious spark sources and seal points of entry. Confirmatory sampling is required to ensure the sealing is adequately protective. Additional response measures at concentrations below 10% of the LEL will be made in consultation with the MPCA. Levels of combustible gas equal to or greater than 10% of the LEL in indoor air warrant fire department notification and control measures. Usually, gas accumulates to such high levels only in confined or enclosed spaces; the fire department can assist in evaluating the source of methane and emergency response actions. The decision to evacuate a building should be made in consultation with the local fire department. Refer to Emergency Response in [Section 1.3](#) for further information. Control measures such as ventilation and/or continuous monitoring should be implemented, and post-mitigation diagnostic sampling and testing is required to confirm performance objectives.

If the source of methane in indoor air is determined to be the result of a utility leak, the property owner or site representative must notify the utility company. The utility company is responsible to aid in addressing the leak, and the MPCA does not have jurisdiction under these instances.

Groundwater

When assessing groundwater contamination, review site indicators such as historical land use records, stressed vegetation, or landfill gas vent measurements. Review available groundwater, soil gas probe, sub-slab, and/or ambient air data, and compare concentrations to the action levels described in previous sections of this document. If groundwater concentrations exceed screening levels (10 mg/L), notify a MN Duty Officer, and take a stepwise approach to installing additional wells and/or soil gas monitoring points in the direction of receptors and downgradient of the release. Evaluate site-specific decisions with the MPCA Project Manager for groundwater concentrations exceeding 28 mg/L. Refer to Emergency Response in [Section 1.3](#) for further information.

4.0 Methane management

The MPCA uses a risk-based approach in evaluating site-specific data and determining appropriate response actions. Response actions may include long-term monitoring, mitigation and/or remediation actions, and/or institutional controls to enforce specific land use restrictions or remedies. Response actions may be implemented during site characterization and will be implemented to address unacceptable risk.

Response actions for indoor air or points of entry are based on detectable gas concentrations at points of entry and indoor air and are not intended to replace a site-specific protocol for responding to combustible gas detected within buildings.

4.1 Long-term monitoring

Initial response actions for methane are completed to mitigate immediate or short-term emergency response and explosive conditions; however, methane generation may be delayed anywhere from weeks to years after a release and persist for decades based on the nature of the methane source and subsurface site conditions. The need for long-term monitoring is evaluated based on site-specific conditions including the results of field screening and analytical data and the nature of the source. Methane gas risk should be evaluated collectively rather than drawing conclusions from one event. Long-term groundwater, soil gas, or indoor air monitoring may be required based on site conditions, including if a source is left in place, or as part of the monitoring of an implemented remedy.

Long-term sampling stations include passive vents, gas extraction wells, gas monitoring probes or points, and continuous-read sensors. Submit long-term monitoring plans to the MPCA for review and approval prior to implementation. Long-term monitoring plans may be subject to change depending on evolving site conditions or construction of new buildings or other receptors.

Monitoring frequency

Acceptable vapor monitoring frequency will vary depending upon site conditions including concentrations and locations in soil gas or indoor air, land use, and the additional response measures in place. In general, monitoring should be conducted at least quarterly; however, methane hazards can change over time and the frequency should be modified accordingly.

Acceptable groundwater monitoring frequency will vary based on detections from the initial investigation and type of site (e.g., bioremediation site). Permanent monitoring wells may be required for periodic monitoring. If groundwater samples exceed 10 mg/L, additional plume delineation and additional long-term soil gas sampling may be required to determine if additional receptors are being impacted.

Field instruments

Follow the manufacturer's instructions for operation, maintenance, and calibration of any field instruments. The instrument selected must have the capability to measure percent methane from zero to 100% by volume to accuracy within plus or minus 0.5%. Keep calibration records with the instrument. The MPCA reserves the right to request these records.

Vapor samples may be analyzed for methane using a range of instruments described in [Appendix D](#). Other fixed gases, including oxygen and carbon dioxide, may require additional instrumentation. Take care to avoid interference with other flammable VOCs. The MPCA recommends an in-line activated carbon filter be used to remove VOCs, so the meter is only reading methane. If you use this option and the reading from the field instrument for the source area does not correlate with the laboratory analysis, resampling for methane, oxygen, and carbon dioxide may be required.

Passive gas vents

Passive gas vents are used to collect and release soil gas and are typically installed at landfills. In addition to venting gas, the vents may serve as soil gas monitoring points. At a minimum, passive gas vents should be sampled once per year to verify that they are functioning as designed.

Active gas extraction wells

Active gas extraction wells also are typically used at landfills and petroleum release sites. These wells are typically used at landfills for active LFG collection and can also be utilized for long-term methane monitoring. Active gas extraction wells should be sampled at least once per month, and sometimes as frequently as once per week, depending upon the consistency of the gas being produced by the landfill. Such monitoring and frequency may also be implemented at petroleum release sites where methanogenesis is occurring.

Permanent soil gas probes

If permanent soil gas monitoring points have been installed for long-term monitoring, a direct reading methane field instrument (e.g., LFG meter) may be used in lieu of laboratory analysis for fixed gases if a good correlation between laboratory and field measurement events can be demonstrated. Refer to [Appendix D](#) for suggested monitoring equipment.

4.2 Mitigation and remediation actions

The MPCA recommends following the MPCA’s program-specific guidance ([MERLA Remediation process and risk-based site evaluation guidance](#), and Petroleum Remediation’s [Risk evaluation and site management decision](#) and [Corrective action design and implementation](#) guidance) when determining appropriate remedy measures. Common considerations in methane remedy selection by media are discussed below. For methane response actions, the primary consideration is the presence of structures or occupied buildings within the methane gas area of concern.

Soil or waste

Waste/source material may have to be excavated and disposed of in a permitted landfill. In this case, the goal is to remove either in whole or part of the source of methane generation. Another common practice is to install passive gas vents. The vents will be installed in or near high concentration areas or serve as a “fence” between the source area and nearby receptors.

Groundwater

Methane will not be removed by common water treatment devices such as sediment filters, water softeners, or carbon filters. The most common remedy solution involves aeration or air stripping, and units range from in-situ to ex-situ. When evaluating response actions for methane in groundwater, consider microbial solutions. For example, isolated pockets of methane could be vented to remove existing methane, and nitrate added to prevent future methanogenesis. The recommended response action will be determined based on site-specific considerations and should be evaluated according to the processes laid out in the program-specific guidance mentioned above.

Vapor

Methane gas concentrations in the sub-slab soil gas exceeding the screening level of 10% of the LEL warrants installation of an intrinsically safe, active ventilation system (e.g., sub-slab depressurization system) in the building or confined space where the elevated methane gas has been detected. If methane gas is detected in sub-slab soil gas exceeding 25% of the LEL, expedited active mitigation is warranted. In the case of indoor air or points of entry, initial response actions for detectable concentrations of methane include sealing points of entry and resampling and may escalate to active mitigation measures, even below 10% of the LEL. Active ventilation may be recommended by the MPCA at lower concentrations if points of entry cannot be properly identified or sealed, or if gas concentrations cannot be mitigated by using other control measures, such as active gas extraction vents. Post-mitigation diagnostic testing is required following implementation of a mitigation system. Further reference may be made to the MPCA [Vapor mitigation best management practices](#) for direction on appropriate mitigation response actions and associated documentation and reporting. Ventilation should be

able to mitigate sub-slab soil gas concentrations and/or indoor air concentrations to at least below 10% of the LEL. If the ventilation system cannot mitigate to these levels, either the ventilation system needs to be modified or other gas mitigation measures need to be implemented. For indoor air mitigation, if 10% of the LEL cannot be achieved, the building must remain unoccupied.

4.3 Redevelopment

Redevelopment at an MPCA remediation site where methane gas has been detected must follow an MPCA approved Response Action Plan (RAP) and Construction Contingency Plan (CCP) or an equivalent program-specific document. The extent and magnitude of methane impacts must be established prior to RAP/CCP submittal. The RAP/CCP must outline the proposed remedy to achieve methane risk-based criteria and program requirements, which may include, but is not limited to, removal of waste material for disposal in a permitted landfill, installation of wells to monitor methane and groundwater, installation of engineered systems to extract/control methane, and installation of a sub-slab depressurization system in a building to prevent vapor intrusion. Refer to the MPCA [Best management practices for development on or near dumps](#) for specific guidance when new construction is planned.

4.4 Institutional controls

An institutional control may be recorded with the property records to ensure the long-term effectiveness of a remedy and/or to limit future exposure to any remaining contamination. An institutional control is not intended to be a sole remedy at a site but rather part of the overall remedy. For a remediation site where elevated levels of methane are present, an environmental covenant and easement (ECE) may be required to:

- [Restrict certain activities at the site that would create an exposure risk to methane.](#)
- [Ensure ongoing operation, maintenance, and monitoring of engineered systems to detect and control methane.](#)
- Notify others (e.g., local government units, prospective purchasers, lenders, tenants, etc.) of the presence of elevated methane at the site and related controls.

For example, a continuous-read combustible gas sensor with alarms may be required at some buildings located near or on a source, particularly if methane has been detected in the buildings. These sensors should be capable of detecting combustible gas at least down to 1% of the LEL for methane (500 ppmv) and alarms should be set to signal or alarm if levels are detected in the range of 10% to 20% of the LEL, depending upon site-specific conditions. An institutional control should be implemented to define the party responsible for the continued operation and maintenance of such equipment. In most cases, the property owner will hold sole responsibility as outlined in an ECE.

Consult with the MPCA Project Manager as institutional controls may vary by program.

5.0 Resources

Below are resources to utilize in determining proper laboratory analysis and QA/QC, additional resources regarding methane response actions and background, and proper and specific MPCA guidance for site-specific conditions (e.g., response actions at landfills, ethanol-based petroleum releases, redevelopment sites, etc.).

Laboratory

Contact the chosen state-approved laboratory to request RLs and MDLs prior to sampling.

MPCA references

MPCA, Brownfield Program, *Best Management Practices for Development on or Near Former Dumps* (c-brownfld4-04). May 2024.

MPCA, Remediation Division, *Vapor investigation and mitigation decision best management practices* (c-rem3-06e). April 2020.

MPCA, Remediation Division, *Vapor mitigation best management practices* (c-rem3-06). April 2020.

MPCA, Remediation Division, *Vapor intrusion assessments performed during site investigations* (c-prp4-01a). July 2022.

MPCA, Petroleum Remediation Program, *Assessment of natural biodegradation at petroleum release sites* (c-prp4-03). January 2021.

MPCA, Petroleum Remediation Program, *Investigation requirements for ethanol-blended fuel releases* (c-prp4-21). August 2022.

MPCA, MERLA, *MERLA Groundwater investigation guidance* (c-rem3-34). TBD 2024.

MPCA, *MERLA Remediation process and risk-based site evaluation guidance* (T c-rem3-33)). TBD 2024.

MPCA, Petroleum Remediation Program, *Soil and groundwater assessments performed during site investigations* (c-prp4-01). March 2024.

MPCA, Petroleum Remediation Program, *Risk evaluation and site management decision at petroleum release sites guidance* (cprp4-02). January 2021.

MPCA, *Greenhouse gas emissions in Minnesota 2005-2020. Report to the Legislature January 2023.*

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ASTM, 2016. *E2993-16: Standard Guide for Evaluating Potential Hazard as a Result of Methane in the Vadose Zone.*

ATSDR, 1998. Investigation of cancer incidence and residence near 38 landfills with soil gas migration conditions, New York State, 1980-1989. Prepared by the New York State Department of Health, Division of Occupational Health and Environmental Epidemiology, Bureau of Environmental and Occupational Epidemiology. PB98-142144.

ATSDR, 2001. Landfill Gas Primer - An Overview for Environmental Health Professionals, Agency for Toxic Substances and Disease Registry, 74 pp.

Eklund, B., 2011. *Proposed Regulatory Framework for Evaluating the Methane Hazard due to Vapor Intrusion*, Environmental Manager, Air & Waste Management Association. February.

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Michigan Environment, Great Lakes, and Energy, 2013. *Guidance Document for the Vapor Intrusion Pathway*. May.

United States Department of Interior (USDOI), 2001. Technical Measures for the Investigation and Mitigation of Fugitive Methane Hazards in Areas of Coal Mining, Prepared by the Office of Surface Mining Reclamation and Enforcement. September.

Appendix A

MPCA-recommended response actions for methane detections

The table presents MPCA-recommended response actions for methane detections in soil gas, sub-slab soil gas, and indoor air/points of entry. Following methane detections, identify the source of methane (LFG, petroleum release, utility gas) and eliminate obvious spark sources. If environmental, notify the MPCA and/or MN Duty Officer depending on concentration and follow steps outlined below. If a utility source, contact the utility company for assistance.

| | Action level | | Response action | Emergency notifications |
|---|-----------------------------------|-----------------------------------|--|---|
| | % of the LEL | Methane % by volume (ppmv) | | |
| Soil Gas (Refer to Section 2.2.1) | <10% of the LEL | <0.5% (<5,000) | Conduct second seasonal sampling event. | No emergency response actions or notifications required. |
| | 10% of the LEL to <25% of the LEL | 0.5% (5,000) to <1.25% (<12,500) | Contact MPCA for technical assistance. Building-specific exterior soil gas OR proceed to sub-slab sampling (below). | No emergency response actions or notifications required. |
| | 25% of the LEL to <50% of the LEL | 1.25% (12,500) to <2.5% (<25,000) | Initiate control measures (eliminate spark source, install ventilation wells) and continue site investigation (including sub-slab sampling) If levels are not controlled to <10% of the LEL, modify mitigation system as needed to meet performance objectives. | Alert the local fire department. |
| | ≥50% of the LEL | ≥2.5% (≥25,000) | Initiate expedited successful control measures and site investigation outlined in the row above. | Alert the local fire department. |
| Sub-Slab (Refer to Section 2.2.2) | <10% of the LEL | <0.5% (<5,000) | Evaluate points of entry using portable field meter and seal identified points of entry. Conduct second seasonal sub-slab soil vapor sampling event. | No emergency response actions or notifications required. |
| | 10% of the LEL to <25% of the LEL | 0.5% (5,000) to <1.25% (<12,500) | Continue site investigation outlined in the row above. Initiate control measures (seal points of entry, install intrinsically safe sub-slab depressurization system). Perform post-mitigation diagnostic and confirmation sampling. If paired indoor air methane concentrations are not controlled <10% of the LEL, modify mitigation system as needed to meet performance objectives and follow applicable Indoor Air row below. | Alert the MN Duty Officer. |
| | ≥25% of the LEL | ≥1.25% (≥12,500) | Immediately initiate control measures and site investigation activities outlined in the two rows above. | Alert the local fire department. |
| Indoor Air (Refer to Section 2.2.3) | <10% of the LEL | <0.5% (5,000) | Evaluate points of entry using portable field meter and seal identified points of entry. Conduct confirmation indoor air sampling and a second seasonal indoor air sampling event. Additional response measures will be made on a site-specific basis. | No emergency response actions or notifications required. |
| | ≥10% of the LEL | ≥0.5% (≥5,000) | Evacuate the building, only trained personnel may enter the building until levels are reduced below 10% of the LEL. Implement response actions in row above. Long-term monitoring is required; confer with MPCA. | Alert the local fire department of potential explosive hazard |
| Confined Space | ≥10% of the LEL | ≥0.5% (≥5,000) | Entry prohibited. Evacuate immediately. | Alert the local fire department (911) and MN Duty Officer. |

Notes: Shaded cells indicate detections requiring Emergency Response actions, refer to [Table 1](#).

Explosive conditions exist between the LEL and UEL. The LEL for methane is 5% methane by volume in air or 50,000 ppmv and the UEL for methane is 15% methane by volume in air or 150,000 ppmv. Exercise care when drilling into areas with potentially high methane concentrations. Intrinsically safe remediation equipment must be used at any site where methane is likely to be present. If field screening identifies methane between the LEL and UEL, **stop work immediately and alert the local fire department**. Methane concentrations resulting in asphyxiation are higher than the explosive concentrations of methane.

Seasonal sampling is required unless detections exceed 10% of the LEL, in which case proceed with immediate response actions or additional sampling (i.e., building-specific soil gas samples or sub-slab vapor samples). Seasons are defined as non-heating (April 1 through October 31) and heating (November 1 through March 31). Sampling and monitoring are expected to be conducted by trained personnel.

Samples should be submitted to a Minnesota-certified laboratory for analysis.

Indoor air monitoring should be conducted with a portable meter by trained personnel at least quarterly. If continuous gas sensors are installed, sensors should be displayed from central locations inside and outside the building.

Appendix B

Reporting methane data relative to MPCA action level

As indicated in [Section 1.3](#), the MPCA uses 10% of the LEL, or 0.5% methane by volume (5,000 ppmv), as an action level for various scenarios. The MPCA recommends that percent of the LEL and ppmv are reported.

The MPCA recommends that tables present concentrations for samples and reference the action level concentration, unless the data are already presented as %v/v in the laboratory report. If the concentrations are given as mass by volume (m/v), the consultant may employ stoichiometric analysis to convert the value of ppmv, as detailed in [Appendix C](#).

When presenting methane data, it is important to understand how different laboratories present the data and how field measurement data, such as % LEL, are presented in reports. An example is presented below:

| Analyte | Sample ID | Sample ID | Sample ID | Action Level |
|---|-----------|-----------|-----------|---------------|
| VOCs | varies | varies | varies | varies |
| Methane | | | | |
| Methane (ppmv) | <26.0 | <30.4 | <27.8 | 5,000* |
| Field Parameters/ Measurements | | | | |
| PID (ppmv) | 3.8 | 4.6 | 0.6 | -- |
| Methane (ppmv) | 20 | 50 | 500 | 5,000* |
| Methane (%LEL) | 0.1 | 0.3 | 1 | 5.0% ** |
| Methane (% by vol) | 0.1 | 0.3 | <u>1</u> | <u>0.5%**</u> |
| Notes: | | | | |
| PID - photoionization detector | | | | |
| ppmv - parts per million by volume | | | | |
| % LEL - percent of the lower explosive limit | | | | |
| * Corresponds to 10% of the LEL | | | | |
| ** LEL for methane, 5.0% methane by volume | | | | |
| **methane by volume corresponds to 10% of the LEL | | | | |

In the table above, the methane concentrations reported in the methane (ppmv) line are correct. However, the results presented on the methane (% LEL) line, outlined in red, are misleading. The table indicates that the data on the methane (% LEL) line represent the percent of the LEL and the action limit is referenced at the end as 5% by volume. This incorrectly suggests that the action level is 5.0% when the action level is 10% of 5%, or 0.5% methane by volume (5,000 ppmv). The corrected version of this is shown in the line outlined in green. This accurate representation of the action level (10% of the LEL presented as 0.5% methane by volume) results in a field measurement identification exceeding the action level (underlined in the green field).

Appendix C

Unit conversions

1 ppmv = 1 volume of gaseous contaminant/1,000,000 volumes of air + contaminant.

| Parts Per Million by volume (ppmv) | Percentage (%) by Volume (VOL) Methane | Percentage (%) by Lower Explosive Limit (LEL) |
|------------------------------------|--|---|
| 1,000,000 ppmv | 100% methane | - |
| 50,000 ppmv | 5% methane | 100% of the LEL |
| 10,000 ppmv | 1% methane | 20% of the LEL |
| 5,000 ppmv | 0.5% methane | 10% of the LEL |
| 1,000 ppmv | 0.1% methane | 1 % of the LEL |

Utilize the ideal gas law (**PV=nRT**) to convert the measured contaminant mass to a volume.

$$P_{air} \times V_{contaminant} = \text{\#moles(contaminant)} \times R \times T_{air}$$

Where,

| | |
|-------------------|---|
| P_{air} | air pressure (kPa) |
| $V_{contaminant}$ | volume occupied by the contaminant |
| T_{air} | air temperature (where $T[K] = T[C]+273.15$) |
| R | universal gas constant = 8.3144 [L*kPa/mol*K] |
| # moles | mass contaminant/molecular weight contaminant |
| 1 atm pressure | 101.325 kPa |

To convert $\mu\text{g}/\text{m}^3$ to ppmv:

$$\text{ppmv} = \mu\text{g}/\text{m}^3 \times (10^{-3}) \times (1/\text{Molecular Weight contaminant [g/mole]}) \times R \times T_{air} \times 1/P_{air}$$

To convert a percentage (%) of LEL to ppmv

$$(\% \text{ LEL reading}) \times (\% \text{ volume at LEL}) \times 100 = \text{PPM at \% LEL reading}$$

To convert ppm to percentage of LEL

$$\% \text{ LEL} = (\text{ppm reading}) / (100 \times \% \text{ volume for LEL})$$

To convert percent methane to percentage of LEL

$$\% \text{ LEL} = (\% \text{ vol} \times 100\% \text{ LEL}) / (5\% \text{ volume})$$

To convert % LEL to % Vol

$$\% \text{ volume} = (5\% \text{ volume} \times \% \text{ LEL}) / 100\% \text{ LEL}$$

Appendix D

Methane field screening/monitoring technologies

Meters are useful for screening and choosing sample placement, but an analytical sample to confirm the readings should be utilized as well, especially in cases where readings are close to screening levels. The field meter must be capable of quantifying the levels of methane gas as a percent methane from zero to 100 by volume, and percent carbon dioxide and oxygen must also be recorded. Quantify methane using the required laboratory analysis in addition to methane field instrumentation during investigation.

A photoionization detector (PID) will not measure methane due to the higher ionization energy (12.6eV). If readings are collected using a calibrated meter as described below, take care to avoid interference from petroleum or other organic compounds. Petroleum and VOCs can cause high readings. A carbon filter which removes these, but not methane, will result in more accurate readings. All explosimeter and some 4-gas measurements will not be valid if the oxygen concentration is less than 19.5% or greater than 21%. For soil gas and sub-slab points, a micro-manometer or landfill gas meter may be used to record pressure readings at each sampling point during each sampling event.

| Type of equipment | Measurement | Principle of operation | Description |
|---------------------------------|---|---|---|
| Combustible Gas Detector | ppm, % LEL, % total gas | Combustible gases change resistance of a Wheatstone bridge. | <ol style="list-style-type: none"> 1. Cannot be used in the presence of silicones, fuming acids, leaded gasoline vapors. 2. Not accurate in low oxygen or high carbon dioxide environments. 3. Relative humidity range 10 - 90%. 4. Zero shift problem in ppm range. 5. Non-selective for gas. |
| Landfill Gas Meter | % methane, carbon dioxide, and oxygen, static and differential pressure | Catalytic oxidation. | <ol style="list-style-type: none"> 1. Designed specifically for use on landfills to monitor landfill gas including extraction systems, flares, and migration control systems 2. Ability to measure static and differential pressure |
| LEL meter/4-gas meter | 1 to 100% of the LEL (~500 ppmv, 5% methane) | Catalytic oxidation. | <ol style="list-style-type: none"> 1. Simple to operate, useful for personal and enclosed space monitoring. 2. Upper limit is only 5% methane. 3. Tendency to overestimate concentration due to cross-sensitivity with VOCs. |
| Infrared Gas Analyzer | 0 to 100% methane, oxygen, carbon dioxide; also reads in % LEL | Computerized infrared analysis. | <ol style="list-style-type: none"> 1. All-weather use from 14°F to 104°F. 2. May be battery operated. 3. Some instruments (e.g., Lantect portable instruments) can also monitor for oxygen and carbon dioxide levels and allow electronic data transfer using a data logger. |
| Flame Ionization Detector (FID) | 0 to 100 ppm to 5,000 ppm total organic vapors | Vapors are burned and the resulting ionization is measured. | <ol style="list-style-type: none"> 1. Will not distinguish between VOCs and other combustible gases, such as methane, without use of GC mode. 2. Not appropriate as a sole real-time monitoring instrument for combustible gases without assumption VOCs are absent. |

| Type of equipment | Measurement | Principle of operation | Description |
|---------------------------------|------------------------------|---|---|
| | | | <p>3. When used in GC mode, there is no temperature control.</p> <p>4. Not intrinsically safe, so use caution if there is a potential for approaching LEL levels.</p> |
| Oxygen Meter | 0% to 25% gas | Atmospheric oxygen is measured on a galvanic cell. | <p>1. Corrosive environments may result in some damaged cells.</p> <p>2. Barometric pressure influences readings.</p> <p>3. Relative humidity range 10 to 90%.</p> |
| Combination FID and PID | 0 to 500 ppm | PID-photoionization lamp ionizes gas and is measured. | <p>1. PID cannot detect methane; FID can detect combustible gases and other VOCs.</p> <p>2. The difference in the two instruments readings.</p> |
| Portable Gas Chromatograph (GC) | Parts per billion (ppb), ppm | Column with FID, PID, or Electron Capture Devices. | <p>1. Required for accurate ppb measurements.</p> <p>2. Common in-field instrumentation for sampling probes.</p> |

Field measurement general procedures

1. The instrument hose should be connected to the probe spigot, then to the instrument pump, and the spigot valves should both be opened simultaneously. The soil gas probe volume should not be evacuated to monitor a worst-case event.
2. The sample shall be drawn with an LFG meter for at least five minutes. In the five-minute period, the maximum methane concentration shall be recorded as percent methane (not as percent of the LEL, refer to [Appendix C](#)). The steady state methane concentration shall also be recorded, if achieved.
3. If no steady state is reached in the original five-minute period, an additional five minutes of test shall be conducted. When the steady state (i.e., variability of less than 5% over a 10-second period) is reached, it should be recorded.
4. If no steady state is reached in the 10-minute period, it should be recorded as “no steady state reading achieved.”
5. At least once during the sampling event, the barometric pressure and ambient temperature shall be recorded. Record other weather conditions and any other pertinent information as appropriate.

In addition to the methane concentration, the percent carbon dioxide and percent oxygen should also be recorded, if available, for every probe.

Appendix E

Quality assurance/quality control considerations

Prior to initiating laboratory sampling, several QA/QC considerations should be accounted for with regards to groundwater and vapor analyses. Project sample requirements should be determined by the project-specific Quality Assurance Project Plan (QAPP) or Sampling and Analysis Plan (SAP), if applicable.

For groundwater and vapor analyses, collect samples according to the appropriate sampling procedures and QA/QC requirements outlined by the state-certified laboratory. **Prior to any sample analysis, confirm appropriate RLs and MDLs for the proposed method.** Obtain laboratory QA/QC specifications from the contracted laboratory. This consideration is especially important for vapor analysis to ensure RLs for methane are low enough to allow comparison to the MPCA's action limit of 10% of the LEL, or 5,000 ppmv methane.

At a minimum, blind duplicates should be collected at a rate of no less than 1 per 20 samples for all media and all analytical parameters. For water samples, trip blanks (for volatiles), field blanks, and equipment blanks should be collected/submitted for analysis for all analytical parameters. Whether matrix spike/matrix spike duplicate samples are necessary, refer to the QAPP or SAP.

Vapor

Ensure that the laboratory's reporting limits for methane vapor are low enough to allow meaningful comparison with the MPCA's action limit of 10% of the LEL, or 5,000 ppmv methane. Laboratory QA/QC should be obtained through the contracted laboratory.

Soil gas samples for fixed gases (methane, oxygen, carbon dioxide, and carbon monoxide) analysis should be collected using laboratory-supplied evacuated canisters. Samples should be collected according to the appropriate sampling procedures and QA/QC requirements outlined by the state-certified laboratory.

EPA Method 3C is a common laboratory method used for the analysis of fixed gases associated with ethanol-blended fuel releases and LFG including oxygen, nitrogen, methane, and carbon dioxide. However, EPA Method 3C has historically resulted in inconsistent methane detections due to RLs which were too high (e.g., exceeding the action level, 10% of the LEL [5,000 ppmv]) to make informed decisions about the data. EPA Method 3C might be appropriate for soil gas samples collected at a methane source, where concentrations are expected to be high, but the method would not necessarily be useful for soil gas samples collected to determine extent and magnitude of methane impacts, for sub-slab soil gas, or indoor air samples to evaluate risk to building occupants.

Blind duplicates should be collected using an appropriate split sampling train, typically provided by the laboratory.

Groundwater

Aqueous samples may be analyzed for methane using a headspace gas chromatography/flame ionization detector (GC/FID) technique based on a method developed by the EPA Robert S. Kerr Environmental Research Laboratory (Kerr Labs). The work is detailed in the standard operating procedure from Kerr Labs (RSK-175). Aqueous samples analyzed for methane using a GC/FID technique based on RSK-175 will require the laboratory to implement additional QA/QC procedures.

RLs and MDLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in the Clean Water Act (40 Code of Federal Regulations 136, Appendix B). The RLs should be three to five times the MDLs. The lowest calibration point in the curve shall be at or below the analyte RL. If the accuracy of the RL standard does not meet the 60% to 140% criteria, new RL standards are chosen and analyzed until the accuracy criteria are met. RLs depend on program needs and may change as new

information becomes available. RLs are verified after each calibration and at least monthly. The RL should be at or below 1 mg/L of methane.

Collect aqueous samples for methane analysis using laboratory-supplied glass serum bottles with preservative consisting of a 1:1 hydrochloric or sulfuric acid to a pH less than 2. Collect samples, at a minimum, in duplicate sets or according to laboratory instructions to guard against loss by breakage and to allow for laboratory QA. The MPCA may also request groundwater samples be analyzed for natural attenuation parameters as described in guidance document [Assessment of natural biodegradation at petroleum release sites](#). Acetate is a degradation product of ethanol and can be used to assess the potential long-term generation of methane in groundwater and may also be recommended for analysis. Consult with the MPCA Project Manager for the site-specific analyses.

General consideration: Batch QC

A batch is defined as up to 20 environmental samples. At a minimum, each batch must contain a method blank and a laboratory control sample/laboratory control sample duplicate (LCS/LCSD) pair. The concentration of methane in the method blank must be less than one-half of the associated RL. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than 10 times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above 10 times the blank contamination will not need to be qualified.

Methane is to be spiked into the LCS and LCSD. The spiking levels should be 5 to 10 times the RLs. The LCS is made from reagent-grade water that has been demonstrated to be methane-free. In a water or soil gas matrix, the percent recovery of methane in the LCS or LCSD must be $\geq 70\%$ and $\leq 130\%$. The relative percent difference (RPD) between the LCS/LCSD pairs in water must be $\leq 30\%$. If prepared, the RPD between water sample duplicate pairs must be $\leq 50\%$. Any QC failure that is not remedied by reanalysis or re-extraction/reanalysis must be flagged in the final report and corrective actions detailed (along with an explanation of the impact on data quality) in the case narrative.