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Evaluating Soil Gas Migration Testing in the Energy Sector

by

Matthew Robert Arthur Day

A Thesis

Submitted to the Faculty of Graduate Studies

Through the Faculty of Science

And in support of the Great Lakes Institute for Environmental Research

in Partial Fulfillment of the Requirements for

the Degree of Master of Science

at the University of Windsor

Windsor, Ontario, Canada

2022

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Evaluating Soil Gas Migration Testing in the Energy Sector

by

Matthew Day

APPROVED BY:

I. Al-Aasam

School of the Environment

J. Gagnon

Great Lakes Institute for Environmental Research

S. O. C. Mundle, Advisor

Department of Chemistry and Biochemistry

August 19th, 2022

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ABSTRACT

Canada's energy sector accounts for approximately 44% of this country's methane (CH₄) emissions, with contributions identified to originate from production infrastructure and natural resource recovery processes. To reduce emissions and mitigate hazards such as asphyxiation, explosions, and groundwater contamination, provincial regulators [e.g., Alberta Energy Regulator (AER)] responsible for regulating the life cycle of oil and gas projects in Canada set guidelines for the identification of gases released from energy sector assets. Diverse field assessment techniques and instrumentation are used by energy sector stakeholders to identify point source emissions. Limited supporting information is available related to the comparative success of the different approaches deployed. This study characterized the reliability of field-deployable gas measurement instrumentation under laboratory and field settings and assessed the applications of these instruments for surface and subsurface gas migration (GM) testing approaches suggested by the AER. The primary focus was to evaluate the most widely available, cost-effective instrumentation, which measures combustible gases with a catalytic combustion detector (CCD). CCD reliability under ideal laboratory conditions was adequate across the concentrations and temperatures typically observed under field conditions. Field applications showed greater variability, likely due to the impact of environmental conditions such as soil moisture, soil compaction, and barometric pressure. [REDACTED]

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LIST OF ABBREVIATIONS/SYMBOLS

AER	Alberta Energy Regulator
BDL	Below detection limit
CCD	Catalytic combustion detector
CO	Carbon monoxide
CO ₂	Carbon dioxide
CH ₄	Methane
C ₂ H ₆	Ethane
C ₃ H ₈	Propane
GC	Gas chromatography
GM	Gas migration
GHG	Greenhouse gas
H ₂ S	Hydrogen sulfide
IR	Infrared
N ₂	Nitrogen
O ₂	Oxygen
O&G	Oil and gas
PPM	Parts-per-million

CHAPTER I

INTRODUCTION

Canada's energy sector is a vital component of the economy and the world's fifth-largest producer of crude oil, accounting for 5% of global crude production (Government of Canada, 2020a). Canada is positioned as a global leader with respect to minimizing the impact of energy production on the environment; however, greenhouse gases (GHGs) released into the atmosphere are thought to have a contributing role in global warming (Dean et al., 2018). The energy sector accounted for roughly 1.7% of global CO₂ emissions, and nationally 26% of Canada's GHG emissions in 2019 were dominated by carbon dioxide (CO₂) and methane (CH₄) (Environment and Climate Change Canada, 2021; Kemfert and Schill, 2009). CH₄ has gained more attention in recent years because it is a potent GHG with a global warming potential 25 times that of CO₂ over a 100-year period (Kemfert and Schill, 2009). The oil and gas industry accounts for approximately 44% of Canada's CH₄ emissions, with agriculture and solid waste disposal accounting for much of the remainder (Dean et al., 2018; Environment and Climate Change Canada, 2016). Resulting from CH₄'s potency as a GHG, action is being taken by the Alberta government to reduce CH₄ emissions by 45% by 2025, contributing to Canada's commitment to the Paris agreement in reducing GHG emissions by 30% below 2005 levels before 2030 (ICF International, 2015; Government of Alberta, 2018). To achieve reduced emissions, the Alberta Energy Regulator (AER) drafted amendments to their Directives 60 and 17 (AER, 2022a,b). These amendments set out to reduce any potential fugitive CH₄ emissions from surface casing vents of active and abandoned oil and gas wells. With estimates of 370,000 abandoned oil and gas wells throughout Canada, the potential for fugitive CH₄ emissions released from surface casing and wellbore failures at even a marginal percentage can lead to notable GHG contributions from the sector (Williams et al., 2021; Kiren et al., 2017; Erno & Schmitz, 1996). Fugitive and vented CH₄ emissions from producing and abandoned oil and gas wells in Canada are estimated to continue at 45 Mt CO₂ per year between 2012 and 2035, with Alberta accounting for the majority (Environment Canada, 2014).

Fugitive CH₄ release from the subsurface to the surface at oil and gas infrastructure (production wells, pipelines, injection wells) is a known issue in the energy sector and has been identified as a concern (Canadian Environmental Protection Agency, 2018; Rostron, 2014). Fugitive emissions released from the subsurface are typically described as a gas migration (GM), where hydrocarbons such as CH₄, ethane (C₂H₆), and propane (C₃H₈) are released from local infrastructure to surrounding soils. Migration of fugitive gases is a concern that requires mitigation because the gases may contaminate shallow aquifers, contribute to GHG emissions, and, in more extreme cases, present an asphyxiation/explosion hazard (Baldassare et al., 2014; Cahill et al., 2017; Osborne et al., 2011; Rowe & Muehlenbachs, 1999). To mitigate GHG emissions and reduce hazards associated with oil and gas infrastructure, the AER set out guidelines for the identification of gases migrating from oil and gas wells. Current regulatory requirements described in AER Directives 20 and 79 (AER, 2014, 2022b) provide helpful guidelines used by service providers offering GM testing services, describing different detection systems and field sample collection approaches. Of the recommended detection approaches, service providers typically choose between infrared (IR) detectors or catalytic combustion detectors (CCDs) when selecting a CH₄ screening device.

Current GM testing approaches largely rely on the use of handheld explosive detectors, e.g., CCDs, which are widely used in GM testing because of their low entry costs, ability to detect multiple gases, and robustness in the field. However, CCDs are typically considered less reliable at accurately identifying the concentrations of gases, such as CH₄, within the lower concentration ranges that are used to dictate the GM status of a tested well. Minimal information is available on the reliability of CCDs when used in a field setting, where environmental factors complicate measurements and affect the reliability of results, and even less so on their ability to identify GM status when paired with various gas sampling approaches (Szatkowski et al., 2002; Mayer et al., 2013). Because of the widespread adoption of CCDs in GM testing, and with most assessment of these devices being performed under ideal laboratory settings, this study aims to identify the reliability of CCDs under both ideal (lab) and typical field conditions as well as understand the effectiveness of various field sampling techniques when using a CCD to identify the GM status of energy sector infrastructure.

1.1 Gas Migration

1.1.1 Gas Migration Classification

Gas migration refers to the movement and transport of gas from its source. In the context of Alberta's oil and gas sector, the AER has defined what is considered a GM, as released from an oil and gas well, in its Directive 87 (AER, 2022d). This Directive classifies GM into two categories based on severity. The first category is denoted as a "serious gas migration," where only one of three conditions must be present: 1) If there is a fire, public safety hazard, or off-lease environmental impact, for example groundwater contamination; 2) If the well was previously abandoned, meaning the well has been cut and capped and production is no longer occurring; or 3) There are producing domestic or agricultural water wells from an unprotected aquifer within a 1 km radius (AER, 2022d). If a well is tested for GM and does not meet any of the above requirements, but there is an indication of gases migrating, i.e., gases observed at the surface and subsurface around the well, it is denoted as a "non-serious gas migration" (AER, 2022d).

1.1.2 Gas Migration Flow Regimes

The migration of gases through the subsurface is generally described by two flow regimes: advection and diffusion. Advection refers to the transport of a gas through bulk motion of the fluid, with gases moving from areas of high pressure to low pressure; this means pressure differentials dictate the direction and rate of gas flow (Phillips & Castro, 2014; Seely et al., 1994). Advection is predominantly how gases are released from infrastructure damage in oil and gas wells due to pressures associated with the connected reservoir (Kiren et al., 2017; Erno & Schmitz, 1996). Proximal to the release point, advective flow is the primary driving force of gas flow to the lower pressure soil surrounding the well (Gao et al., 2021), where gases spread laterally and vertically and contribute to aquifer contamination (Videc et al., 2013), explosive conditions in soil gas (Kelly et al., 1985), and the addition of GHGs into the atmosphere (Bachu et al., 2017; Forde et al., 2018). In contrast, diffusion is a process in which concentration gradients rather than pressure gradients act as the driver for migration (Kruczek, 2016). Diffusion

can act both independently and cooperatively with advection to drive the migration of gases. Diffusion becomes the driving force for GM after pressure gradients weaken further away from an infrastructure failure (Gao et al., 2021).

1.1.3 Role of Soil Properties in Gas Migration

GM is primarily influenced by pressure and concentration gradients but also by environmental factors that can vary between sites, or even from day-to-day (Phillips & Castro, 2014; Kruczek, 2016). Near-surface soils, through which gases flow through before breaching the surface, play an important role in GM. Soil type and properties influence how gases will migrate through the subsurface. Soil permeability describes the ease with which a fluid flows through a soil and largely correlates to the tortuosity of flow paths and gas flow-through rates (Niya & Selvadurai, 2018). Low permeability soils can be described in terms of the level of soil heterogeneity, size of soil grains present, and compaction state (Smith, 2006; Chapuis, 2012). Such variables largely influence the void space between soil grains, where a decrease in void space is associated with a significant decrease in permeability; however, scenarios do occur in which the degree of void space, termed the porosity, is not the only variable influencing soil permeability (Dolzyk & Chmielewska, 2014).

1.1.4 Role of Soil Moisture Content in Gas Migration

Soil moisture content refers to the relative amount of water filling in the pores or void space of a soil (Civeira, 2019) (Figure 1a). During rainfall events, the infiltration of rainwater into the subsurface allows for the temporary increase in soil gas surface flux through the displacement of existing soil gas (Koorevaar et al., 1983). However, after a rainfall event the moisture can be retained in the soil pores for extended periods, depending on the soil type and drying conditions (Li et al., 2016) (Figure 1b). The amount of diffusive gas transport can be reduced substantially when soils have elevated soil moisture content, as gas phase molecular diffusion is approximately 10,000 times faster than aqueous diffusion (Whalen et al., 1990). This causes complications to typical soil gas flow pathways and contributes to the trapping of gases in blocked pores, which

has been observed to play a dominant role in increasing observed subsurface soil CH₄ concentrations (Gao et al., 2021). In addition to reduced diffusion rates, moisture content can influence advective flow pathways, causing increased tortuosity and further lateral migration of fugitive gases from an infrastructure rupture point (Benevente & Pla, 2018) (Figure 1a). This effect is further evident in soil types that can hold larger volumes of water (Figure 1b), with soils featuring smaller grain sizes having a larger capacity to retain water and soils with larger grains behaving in the opposite manner (Arya & Paris, 1981).

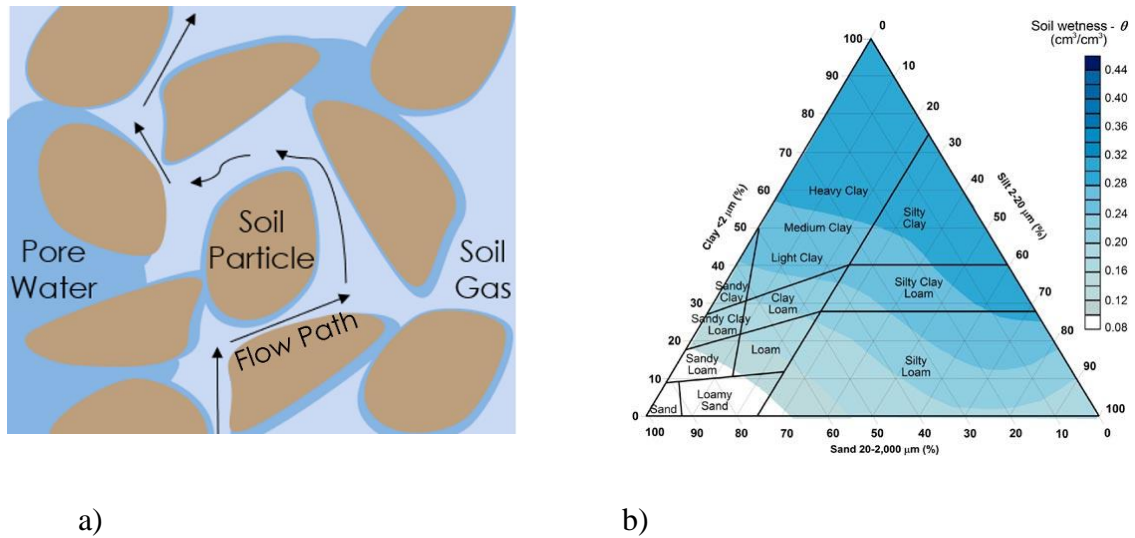


Figure 1: (a) Visual representation of the influence of soil moisture on advective flow pathways. (b) Representation of various soil types and their capacity to hold moisture relative to their total volume based on ratios of grain sizes. From https://www.terragis.bees.unsw.edu.au/terragIS_soil/sp_water-soil_moisture_classification.html (retrieved 2022).

1.1.5 Role of Barometric Pressure in Gas Migration

Barometric pressure is the measurement and representation of the pressure exerted by the weight of air in the atmosphere at a given location on the Earth's surface.

Barometric pressure can vary spatially and temporally, largely due to density shifts associated with local temperatures. Colder, denser air will result in higher barometric pressures, while warmer, less dense air results in lower barometric pressures (B., 1918). Local topographic elevation will also influence barometric pressures; for example, sea level will typically be at higher barometric pressure compared to mountain tops because the amount of air exerting force at the Earth's surface decreases with altitude (B., 1918;

Forde et al. 2019). A common scenario influencing temporal shifts in barometric pressure is the introduction of a storm front, where air from two regions collides, causing the warmer, less dense air to rise and create a vacuum effect that will locally decrease observed barometric pressures (B., 1918; Forde et al. 2019). Of greater importance to GM studies is the observation of diurnal barometric changes, with pressures increasing at night when the air cools and becomes denser and then decreasing during the day when daily temperatures peak and atmospheric gases expand (Forde et al., 2019). All of the above causes of barometric pressure shifting can lead to a process known as ‘barometric pumping’, where the decrease/increase of atmospheric pressure can influence the strength of pressure gradients between soil gas in the subsurface and the Earth’s surface. A decrease in barometric pressure can strengthen such a gradient and allow for the release of fugitive gases to the surface or enhance already existing surface efflux, while an increase in barometric pressure can cause the inverse effect where a downward displacement of gases can occur (Massmann & Farrier, 1992; Forde et al., 2019) (Figure 2). Despite the potential influence on soil efflux rates, barometric pressure is rarely considered in GM investigations, likely due to high day-to-day variability that cannot always be accounted for when planning a GM investigation.

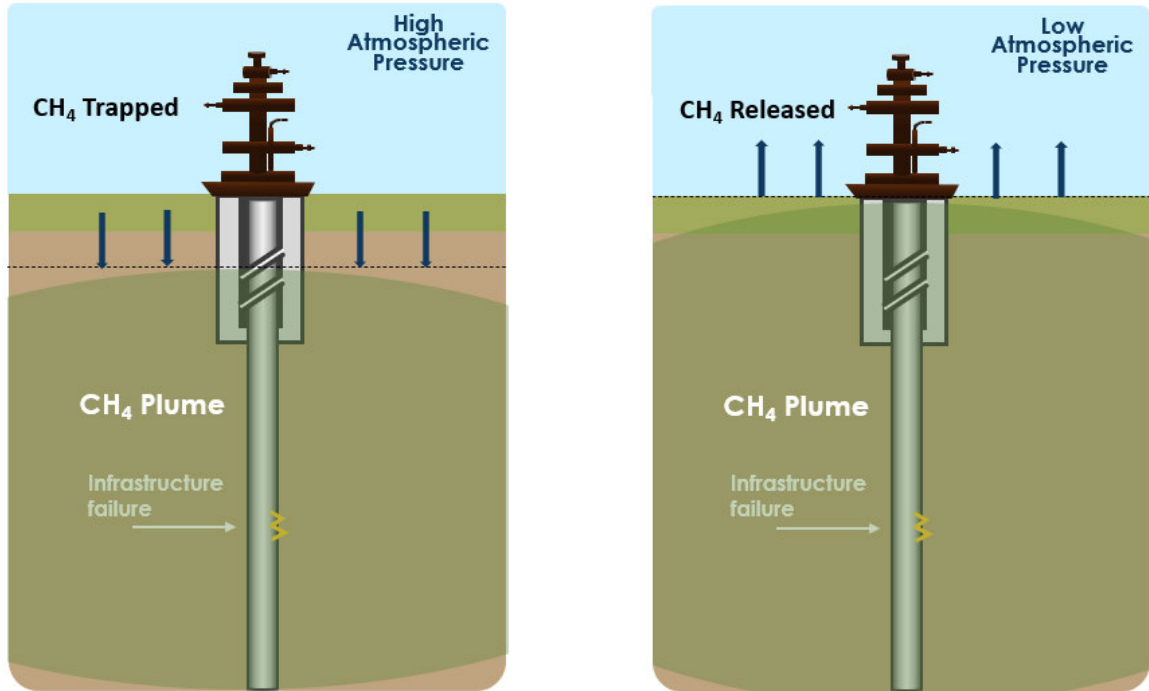


Figure 2: Schematic of the barometric pumping effect on soil gas observed at an oil and gas infrastructure failure: trapping of gas below surface during barometric high (left) and release of gas during barometric low (right).

1.2 Current Procedures for Gas Migration Testing

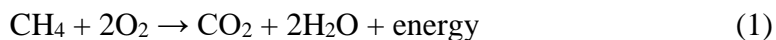
Current approaches to GM testing laid out by the AER are broad and cover a wide range of potential factors influencing GM; however, less focus is directed at the quality of sampling and analytical approaches used for detecting gases found at active gas migration site (AER, 2022b). Licensees have requirements based on temporal factors when performing testing: they must begin in frost-free months, avoid periods immediately after rainfall, and prevent water and ice from potentially blocking the flow of gas to the surface and impacting the result of the GM investigation (AER, 2022b). Background work must also be done at each site, with the soil horizon examined to ensure the site is not contaminated with volatile compounds such as diesel fuel, solvents, or oil, which may breakdown into CH_4 and influence detection readings and site interpretation (AER, 2022b). Surface sampling involves using a calibrated explosive meter, described as a CCD, at two points 30 cm from the wellbore on each side. Tests are

also conducted at 2 m intervals outwards up to 6 m in each cardinal direction from the wellbore or to where vegetation stress is identified (AER, 2022b). If CH₄ is detected at surface sampling locations, subsurface sampling is required. Subsurface testing begins with boring a hole 50 cm in depth with a diameter of 64 mm. The probe of a CCD is then inserted into the borehole and the surface is covered to reduce atmospheric interactions as the sample gas is drawn from the hole. In doing such, ground disturbance requirements described in the Alberta Pipeline Act must be followed (Province of Alberta, 2021). Current AER procedures for GM testing provide valuable ‘common sense’ approaches for service providers; however, further optimization may still be required to increase the effectiveness of such procedures.

1.3 Catalytic Combustion Detection

To diagnose active and abandoned wells that are potentially releasing fugitive CH₄, the AER sets out guidelines in their Directive 20 that detail various identification techniques (AER, 2022b). A focus of the Directive is the utilization of “explosive” detectors to identify hydrocarbons that are typically only found in association with a nearby well. More specifically, CCDs are used to identify the concentration of CH₄ relative to its lower explosive limit (LEL), at depths of at least 50 cm below the surface radially around the well in question (AER, 2022b). A CCD works on the basis that oxidation of a hydrocarbon gas is an exothermic reaction (Wang et al., 2011). A sensor then detects the increase in temperature associated with the reaction and converts it to a signal that is proportional to the gas concentration (Government of Canada, 2020b; Wang et al., 2011). Typically, the active element is embedded within a catalyst, with the reaction taking place on the surface of a catalyst that reduces the activation energy required for the reaction to take place (Government of Canada, 2020b). Additionally, combustible gases entering a CCD are required to react exothermically with oxygen for the essential change in temperature that is used for their measurement (see Eq. 1 for an example hydrocarbon combustion reaction involving methane) (Government of Canada, 2020b; Wang et al., 2011; RKI Instruments, 2019). Handheld CCDs are a staple in environmental field sampling and have many advantages such as cost effectiveness, ease of use, and robustness (Government of Canada, 2020b). However, limitations include

sensor poisoning from corrosive gases and oxygen requirements for catalytic reactions to create the temperature variances that are used to sense the gases (RKI Instruments, 2019).



Oxygen requirements aside, a CCD works based on changes in heat to obtain information about the concentration of gases present (Government of Canada, 2020b). As such, irregularities in temperature have the potential to influence the concentrations of observed gas readings by the device itself and may lead to an over/underestimation of the severity of a potential GM issue. Example scenarios exist in fall sampling seasons when seasonal/local temperatures begin to decrease towards 0 °C, while still within the timeframe of spring-to-fall AER sampling guidelines (AER, 2022b), or even within the course of a day. These cool temperatures provide a scenario in which a handheld CCD can be colder prior to and during sampling, with cooler condensed gases reacting with a warmer detector, or warmer, less condensed gases insulated by a warmer subsurface. A reference sensor is widely used in handheld CCDs to account for general background fluctuations that may influence observed CH₄ concentrations (RKI Instruments, 2019).

1.4 Infrared Gas Detection

In contrast to CCDs, infrared (IR)-based detectors are also commonly used for the detection of fugitive CH₄ in GM investigations. However, IR detectors have no concentration limitations with respect to the gases they can detect. An IR detector can detect CH₄ concentrations of up to 100% versus the CCD limit of 5% (100% LEL); IR detectors are also not bound to the same oxygen requirements, nor are the sensors vulnerable to poisoning by acid gases such as hydrogen sulfide (H₂S) (Aldhafeeri et al., 2020; Government of Canada, 2020b; RKI Instruments, 2019). Although concentration ranges of IR detectors are much wider than for CCDs, the added value to an actual GM investigation is unclear because a GM would still be classified as serious at the detection limit of a CCD (5% CH₄). IR detectors are more expensive than CCDs and are less robust to factors such as humidity, temperature, and wind speed that affect the performance of the sensor (Aldhafeeri et al., 2020; Government of Canada, 2020b). IR techniques provide CH₄ concentrations rather than a bulk combustible gas measurement; however,

minimal information is available on the ability of optical filters within handheld IR devices to distinguish between absorption frequencies of alkane species with comparable chemical functional groups and IR frequencies commonly found in oil and gas infrastructure (CH_4 , C_2H_6 , C_3H_8 , etc.). Due to the robust and inexpensive nature of handheld CCDs, they are commonly the first choice for field operators in the GM space, and thus understanding the limits and capabilities of these devices in the context of actual GM investigations should be a priority for identifying best practices.

1.5 Gas Blending

The requirement of O_2 for catalytic reactions to occur can provide gaps in the testing of handheld CCD instruments across a range of CH_4 concentrations that still contain the minimum O_2 threshold of 10% (RKI Instruments, 2019). Finding multiple gas standards across a range of CH_4 concentrations that contain sufficient concentrations of O_2 may introduce logistical and financial constraints, reducing the cost-benefit of performing what would normally be an inexpensive and simple set of tests. However, these issues are easily avoided when portable gas mixers are used. Portable gas mixers can mix gases down to the ppb level (GOW-MAC Instrument Co., 2018), reducing the number of gas standards used when testing various gas detection approaches. Gas blending using such technology is achieved by manipulating the flow rate of both a dilutant and dilution gas to achieve a gas concentration anywhere below that of the dilutant gas, within the defined operational capability of the device (GOW-MAC Instrument Co., 2018).

1.6 Study Objectives

CCDs are currently used to diagnose wells with potential GM issues on a large scale due to their cost effectiveness, robust nature, and ease of use (Government of Canada, 2020b). However, limited testing has been performed on the reliability of such instruments in the context of GM investigations. This study aimed to provide insights into best practices for GM investigations by defining the error in measurement capability of handheld CCDs under ideal laboratory conditions. This included testing performed at the

lower detection limits of CH₄, detector linearity, accuracy, and precision compared to GC approaches. The reliability of CH₄ detection using a handheld CCD was then tested through observations made in a typical field setting at conventional oil and gas operations and compared to those made in a controlled laboratory setting. The second objective was to provide insight on the AER approaches currently used in GM investigations to identify potentially leaking oil and gas wells. This included surface CH₄ detection with and without the use of soil gas domes, as well as subsurface testing using soil gas probes and augured boreholes. This involved an evaluation of GM investigations conducted through surface detection alone, determining the quality of data produced using current subsurface detection approaches, and identifying potential temporal factors that may influence such detection.

CHAPTER II

MATERIALS & METHODS

2.1 Catalytic Combustion Laboratory Testing

2.1.1 Sample Gas Preparation

Sample gases were prepared at CH₄ concentrations between 500 ppm and 1.5% v/v, ensuring concentrations of each sample had the minimum O₂ requirement (10% v/v) for catalytic combustion in the device to occur. A portable gas blender (Figure 3) was used to prepare the sample gases, where both 1% and 3% CH₄ standards in molecular nitrogen (N₂) were diluted using compressed air that contained 21% O₂. The gas blender drew gas at calculated flow rates from both the CH₄ standard and dilution gas (compressed air) using the dilution calculation described in Eq. 2 to achieve the desired concentration (GOW-MAC Instrument Co. 2018). By inputting the concentration of CH₄ in the gas standard, desired CH₄ concentration, and flow rate of the gas standard, the required flow rate of the dilution product was determined. Flow rates for the dilution and sample gases used are described in Table 1. After the desired gas concentrations were achieved, samples were then directly transferred to 3 L Tedlar bags from the gas blender using a three-way Swagelok valve to reduce air contamination. Tedlar bags (in triplicate) were filled and purged with the desired gas, then filled to 75% capacity before analysis. Additionally, one set of samples was refrigerated for 24 h to achieve temperatures of approximately 3 °C and simulate colder field settings.

$$C_i = \frac{Q_s}{Q_s + Q_d} \times C_I, \quad (2)$$

where C_i is the concentration of component i in the diluted sample, C_I is the concentration of component I in the original sample, Q_s is the sample flow rate, and Q_d is the dilution flow rate.

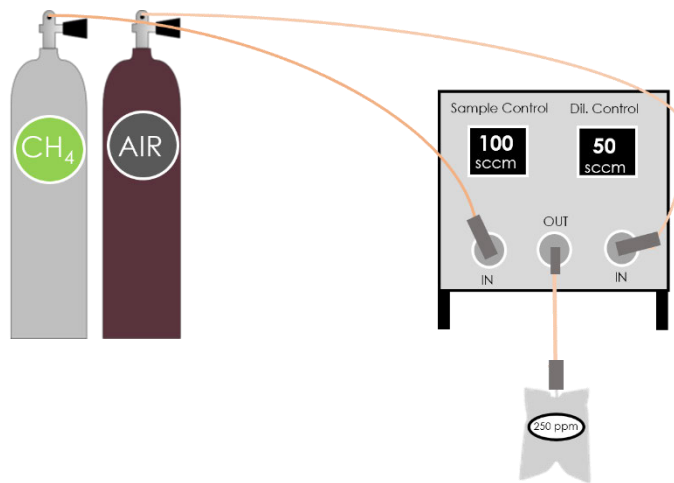


Figure 3: Visual representation of the portable gas blender approach utilizing CH₄ and compressed air to achieve desired CH₄ concentrations.

Table 1: Flow rates used with the portable gas blender to achieve the desired CH₄ dilutions.

Desired CH ₄ Concentration (ppm)	Methane Standard (ppm)	Sample Gas Inflow Rate (sccm)	Dilution Gas Inflow Rate (sccm)
250	10000	20	780
500	10000	30	570
750	10000	36	444
1000	30000	35	315
1500	30000	36	204
2000	30000	35	490
3000	30000	35	315
4000	30000	34	221
5000	30000	35	175
6000	30000	35	140
7000	30000	35	115
8000	30000	32	88
9000	30000	33	77
10000	30000	30	60
15000	30000	35	35

2.1.2 Sample Gas Analysis

The RKI Eagle II handheld CCD (RKI Eagle II; RKI Instruments) was chosen for sample gas analysis because of its widespread use by service providers and was configured with a catalytic combustion sensor designed to detect O₂, CO₂, H₂S, and CH₄, with a detection limit of 5% v/v CH₄ (100% LEL). Manufacturers outline effective operation between temperatures of -20 to 50°C and humidity levels between 0-100%, with a standard measurement error of 5% (RKI Eagle II, RKI Instruments). The handheld CCD was calibrated using a demand flow regulator set to the manufacturer's suggested calibration gas mixture of 2.5% CH₄, 12% O₂, 25 ppm H₂S, and 50 ppm CO, replicating a typical calibration prior to field operation of the device. After being filled with CH₄, sample bags were connected to the handheld CCD using silicone tubing and a three-way Swagelok to prevent any low-flow errors in the device and allow samples to be drawn with minimal air contamination. The device was left to read for approximately 15-30 s, i.e., the point at which stable readings were recorded for CH₄ and O₂. To simulate lower temperatures that may be typical within early or late field seasons, the detector was cooled to approximately 3°C over a 12-h period in a refrigerator, then taken out briefly for the analysis of room temperature gas and 3 °C cooled gas at concentrations of 250, 500, 750, 1000, and 1500 ppm. The device was then returned to the refrigerator and cooled between each gas sampling event. Prior to each handheld CCD reading, 50 mL of sample gas were drawn from each triplicate Tedlar bag via a 50 mL syringe with a two-way lock and ran in triplicate utilizing a gas chromatograph (GC) for each separate triplicate Tedlar bag. Samples were drawn from the bag itself rather than directly from the gas blender to ensure any air contamination was accounted for when determining the effectiveness of the handheld CCD.

2.2 Gas Migration Field Sampling

2.2.1 Surface Gas Detection

A handheld CCD was used to identify the concentrations of gases, particularly CH₄, observed at the surface-subsurface interface. Sampling approaches were consistent

with approaches widely used in GM testing under AER Directive 20 guidelines (AER, 2022b). The first approach was performed by holding the probe of the device approximately 3 cm above the interface and then the observed reading recorded after 15-30 s, i.e., after the reading had stabilized. This approach continued at 1 m intervals in each cardinal direction away from the well centre up to 6 m, i.e., beyond the 2 m interval required by AER Directive 20 guidelines (AER, 2022b) (Figure 4). A secondary approach was used in a previous investigation performed in 2019 to reduce the influence of wind speed and external gas sources using a subset of surface domes. On the dome a sampling port was made with a two-way syringe lock attached to silicone tubing. The domes were inserted approximately 3 cm into the ground and gases were allowed to equilibrate for 30 min before a handheld CCD was attached to the sampling port and a reading recorded (Figure 4).

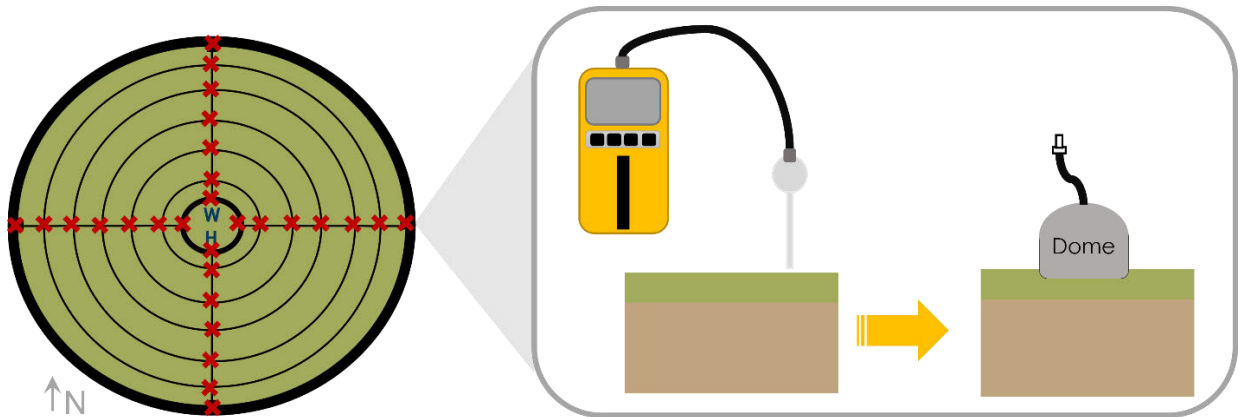


Figure 4: Representation of surface methane detection approaches used, showing a handheld CCD detecting surface efflux by holding the probe above the ground interface (left) and the placement of the surface dome (right).

2.2.2 Subsurface Gas Detection

A variety of approaches were used to obtain data on subsurface concentrations of CH_4 and other gases. The first approach used holes augured into the subsurface at the maximum allowable depth before a ground disturbance permit is required (30 cm). This approach exclusively involved measurements taken using a handheld CCD. Once holes

were augured, the handheld CCD probe was inserted, and a weak seal created between the filter of the device and the top of the hole to help reduce atmospheric interactions. This approach is consistent with current AER Directive 20 guidelines for subsurface CH₄ detection (AER, 2022b). The second and main approach used 12” soil gas probes to collect data with minimal atmospheric contamination. Probes were inserted to a depth proximal to 30 cm, sampling ports then sealed with silicone tubing and a two-way Swagelok, and gases allowed to equilibrate over 30 min. After equilibration, a field-dedicated GC or handheld CCD was used to measure concentrations of subsurface gases (Figure 5). To sample gas from the probe for the GC, a 50 mL syringe with a two-way lock was attached at the probe sampling port and a sample was drawn. Careful consideration was given to drawing a sample slowly so as to not create a strong pressure differential between the surrounding soil gas and the probe after equilibration. Once a sample was collected, it was promptly analyzed by the field GC configured with a thermal conductivity detector (TCD). At select locations, soil gas probes were also sampled using a handheld CCD, with the device probe hooked up to a two-way valve on the soil gas probe. Peak readings from the handheld CCD were then recorded. After field GC analysis, any probe samples that contained over 3000 ppm CH₄ or CO₂ were subsampled into either 30 or 50 mL bottles and sealed with a rubber butyl stopper. Discrete samples were taken to validate gas concentrations and for further analysis in the laboratory.

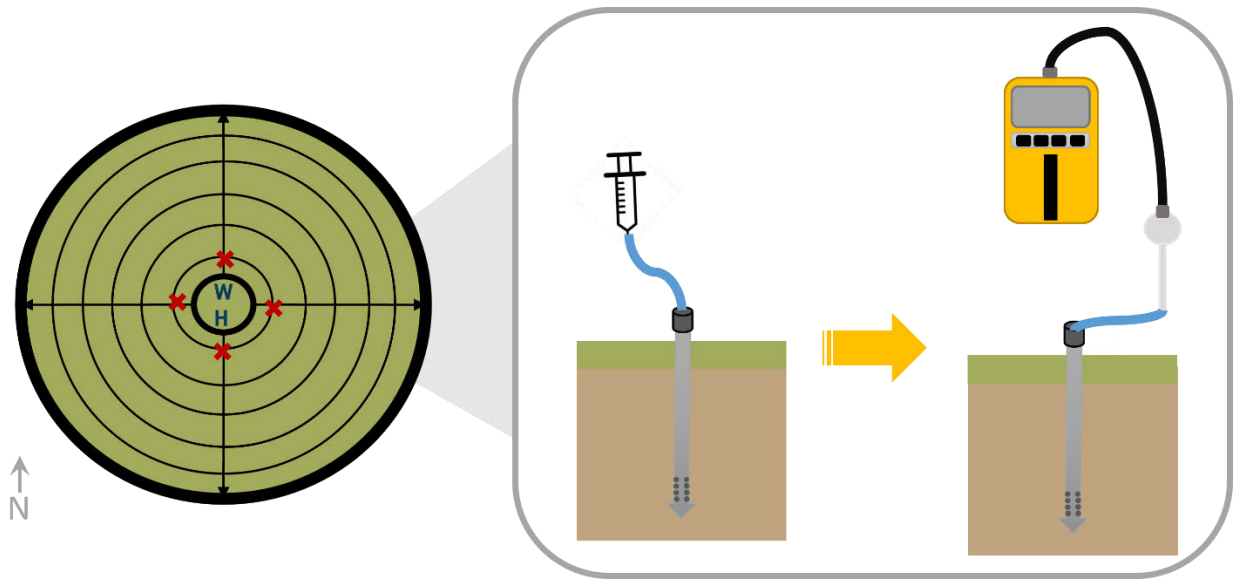


Figure 5: Representation of subsurface methane detection approaches used, showing a probe inserted to a depth proximal to 30 cm with sample then analyzed by a handheld CCD or collected for field GC analysis.

2.2.3 Subsurface Moisture Sampling

To understand the influence of soil moisture on GM status, soil moisture readings were taken promptly after, and next to, soil gas sampling locations. The probe was placed approximately 10 cm below the surface to reduce impacts from shallow vegetation and to gather a sample more representative of the soil profile. Soil moisture conditions were identified using a Delta-T SM150 soil moisture kit, with a SM150T moisture sensor hooked up to an HH150 moisture meter, configured to a mineral-type soil. Given the soil type in the sample areas was defined as a brown chernozemic soil and assuming an approximate soil porosity of 0.4, soil moisture values would range from ~0-40% v/v, with 40% soil moisture representing full saturation, and the remaining 60% representing packed soil contents (Canadian Society of Soil, 2020; Etnyre, 1989).

CHAPTER III

RESULTS & DISCUSSION

3.1 Laboratory Testing

3.1.1 Accuracy and Precision of Catalytic Combustion vs. Gas Chromatography

Identifying potential GM events from energy infrastructure requires the use of analytical instrumentation to quantify the presence of CH₄ being released from soils. However, various types of analytical tools are used when performing site assessments. Typically, three detection approaches are used: CCD, IR, and GC, each with their own benefits. Catalytic combustion measures a bulk combustible gas concentration, provides a cheap, robust, widely available, and portable platform for gas detection, and requires minimal training to use. IR detection provides the same benefits as catalytic combustion with a trade-off in cost but gains in terms of a broader detection limit for CH₄ (0-100 v/vol%). IR detectors typically provide an accuracy of ±10% and detection range that is greater than for CCD detectors (Heath Consultants Incorporated, 2019). When identifying the presence of a GM, concentrations detected above the 5% CH₄ threshold of a CCD lead to the same conclusion; however, the accuracy of portable gas detectors near lower detection limits (10-2000 ppm) provides more value when determining whether a site has GM status as defined by the AER or not. Further, minimal information is available on the accuracy of handheld IR detectors within CH₄ ranges that may dictate whether a GM is present (e.g., 10-2000 ppm). Additionally, IR provides a measure of CH₄ concentrations rather than bulk combustible gas; however, minimal information is available on the ability of optical filters within handheld IR devices to distinguish between absorption frequencies of alkane species with comparable chemical functional groups and IR frequencies (CH₄, C₂H₆, C₃H₈, etc.). Compared to catalytic combustion and IR approaches, GC is the most species-specific approach for identifying concentrations of gases. Although GC can often provide the most reliable results across concentration ranges, it is less accessible to the service sector due to high initial infrastructure costs and

added expenses associated with bringing a trained technician to a field setting, lack of portability, the requirement of numerous calibration gases, and more maintenance. The higher costs and technical knowledge needed to use GC, positions catalytic combustion as the typical instrument of choice of many service providers. As such, understanding how CCDs compare to GC across lower concentration ranges that are typically used to identify the presence of a GM (1000-15000 ppm) may provide the strongest indicator of CCD effectiveness. Further, errors in measurements made at the 1000 ppm mark are of greatest importance because over/under representation of gases at this threshold may lead to the misclassification of GM status at oil and gas infrastructure.

The handheld CCD showed varied levels of success when compared to the GC. At lower concentrations of CH₄ (1000-5000 ppm), readings were between 267 to 633 ppm above the expected concentration of respective mixtures, representing an experimental error of 13 to 26% (Table 2). Although a high degree of error is associated with low concentration CH₄ mixtures, in the context of a GM investigation, CH₄ readings above 1000 ppm would in most cases indicate a potential GM issue and therefore this method would meet the intended objective of GM identification. The accuracy of detection for higher concentrations of CH₄ was also determined to gain preliminary insight into the potential risk and severity of a GM. CCDs have an upper threshold detection limit of 5% (100% LEL), which is well above the concentration needed to identify a potential GM issue and reflects a more serious concentration of gas. The additional precision and accuracy gained above 100% LEL using IR approaches ultimately does not provide information that will change the interpretation for this application. As the concentration of gas mixtures increased to 6000-8000 ppm, the absolute value above expected slightly increased (533-667 ppm) while the error dropped to 8-10%. At the higher range of tested concentrations (9000-15000 ppm), the absolute difference slightly increased again (450-833ppm) but the error dropped to below 5%. With increasing accuracy in mid to higher concentration ranges, the CCD begins to provide results more closely resembling GC approaches. As expected, the GC was quite accurate across all concentration ranges, with readings at most 3% above expected values (Table 2). Further, when comparing the values obtained from the handheld CCD and GC, the GC is marginally more accurate (by at most 3%).

Table 2: Expected and measured concentration of analyzed gas mixtures, and the differences between them, using catalytic combustion and gas chromatography.

Expected [CH₄] (ppm)	CCD [CH₄] Observation (ppm)	Difference: CCD – Expected (ppm)	GC [CH₄] Observation (ppm)	Difference GC – Expected (ppm)	Difference CCD – GC (ppm)
1000	1267 ± 76	267 (27%)	1029 ± 48	29 (3%)	237 (23%)
2000	2383 ± 29	383 (19%)	2063 ± 105	63 (3%)	320 (16%)
3000	3467 ± 76	467 (15%)	3043 ± 110	43 (1%)	423 (14%)
4000	4500 ± 50	500 (13%)	4039 ± 110	39 (1%)	460 (11%)
5000	5633 ± 189	633 (13%)	5121 ± 30	121 (2%)	511 (10%)
6000	6583 ± 57	583 (10%)	6109 ± 95	109 (2%)	474 (8%)
7000	7533 ± 189	533 (8%)	7118 ± 84	118 (2%)	414 (6%)
8000	8667 ± 173	667 (8%)	8144 ± 133	144 (2%)	522 (6%)
9000	9450 ± 520	450 (5%)	9040 ± 315	40 (0.5%)	410 (5%)
10000	9833 ± 722	833 (2%)	9835 ± 509	177 (2%)	2 (0.02%)
15000	15583 ± 15	583 (4%)	15363 ± 374	363 (2%)	220 (1%)

CH₄ readings using the CCD were reasonably accurate at lower concentrations and the reproducibility of measurements was very good. The linearity of concentrations observed using the CCD relative to the expected concentration was characterized by an R² of 0.998 (Figure 6a); the corresponding value for GC analysis was 0.999 (Figure 6b). Both approaches provided reproducible readings; however, the CCD provided readings closer to the expected gas concentrations when above concentrations of 8000 ppm while the GC was accurate across all observed concentrations. Notably, the CCD uses a single point calibration at 2.5% (50%LEL) CH₄ and the observation that accuracy falls as the concentrations decrease from the calibration concentration is not surprising. Comparatively, GC uses a series of calibration points that contribute to its performance across a larger concentration range. The good agreement in terms of the linearity in concentration measurement demonstrated in this study suggests the handheld CCD performs well and, despite greater error in measurement, is suitable for GM applications.

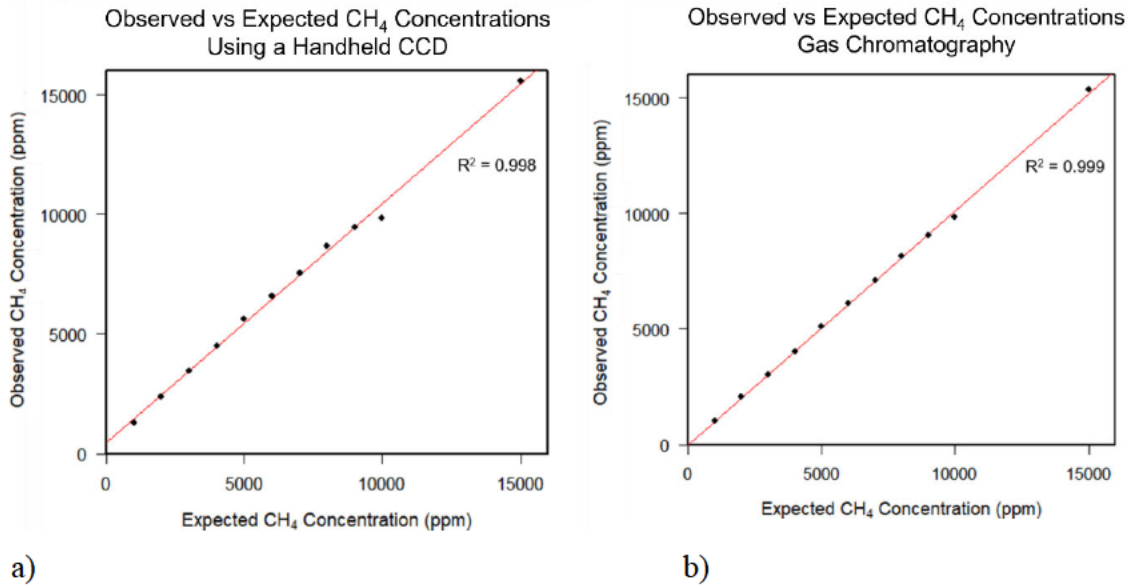


Figure 6: Observed methane concentrations using catalytic combustion (a) and gas chromatography (b) versus the expected concentration of gas mixtures.

3.1.2 Defining Measurement Error Associated with CCD

Scenarios may exist in GM investigations in which subsurface CH₄ concentrations can be near a decision-making threshold for identifying a GM issue. Error in measurement raises concerns that an overrepresentation of gases present may lead to a false positive GM identification, or underrepresentation to a false negative GM identification. To avoid the financial liability of both outcomes, understanding the reliability of CCDs and determining the level of measurement error is of importance. The CCD showed a high degree of reproducibility for CH₄ measurements with concentrations above 1000 ppm, but readings were less accurate for concentrations below 8000 ppm. This study suggests CCD measurements below 5000 ppm will likely have errors of $\sim \pm 500$ ppm, and those above 5000 ppm will have errors of $\sim \pm 1000$ ppm in practice. In the GM investigative platform, these error thresholds represent the largest difference between expected and observed measurements of CH₄ needed to definitively account for the change in output increments on a typical handheld CCD. Such error ranges may reduce the quantification ability of these devices; however, it is important to note that GM status within these thresholds would remain the same, and so these errors have little impact with respect to the identification of a potential GM issue.

3.1.3 Reliability of Catalytic Combustion with Temperature

The CCD showed comparable performance to GC approaches in CH₄ detection when testing was performed under an ideal (lab) scenario in which environmental conditions such as temperature and humidity were controlled, and the detector provided with an adequate supply of O₂ and gas volume. However, such conditions are typically not the case in a field setting. To account for temporal variation in environmental conditions, the AER GM testing guidelines suggest that sampling occur in frost free months. However, even within “frost free” months, large temperature variations can occur between spring and fall sampling seasons. Controlling for all temporal variables found in a field setting is near impossible but understanding the potential impacts of temperature on a CCD is important. A typical CCD determines concentrations based on relative changes in resistivity within the device caused by heat generated from the catalytic combustion of CH₄. As such, temperature variations outside the device may influence observed resistivity within the device and potentially reduce detector reliability. As shown in Table 2, the largest error in CCD measurement was at CH₄ concentrations of ~1000 ppm, which is an important concentration threshold for GM identification. Because the greatest variability occurred at these low CH₄ concentrations, testing to assess temperature effects on CCD performance were performed for a CH₄ concentration range of 250-1500 ppm; this also provided additional insight into detector performance at concentrations near the AER minimum detection limit for CCDs (500 ppm) (AER, 2022b).

CH₄ values measured within the lower sensing capability of the CCD (250-1500 ppm) showed a standard deviation ranging from 13 to 58 ppm (Table 3) when device and gas temperatures were slightly above freezing (3 °C). The reproducibility of measurements, as a percentage, generally increased as the expected concentrations rose. However, this trend was also observed in previous experiments conducted at room temperature (Table 3). A standard deviation of 16% (58 ppm) was observed for an expected CH₄ concentration of 250 ppm, down to 5% (32 ppm), 1.3% (13 ppm), 1.2% (16 ppm), and 1.8% (34 ppm) for expected concentrations of 500, 750, 1000, and 1500 ppm, respectively; these values represent a greater degree of reproducibility compared to room

temperature testing. The greatest variability is observed at the lowest CH₄ concentration tested (250 ppm). At such low concentrations, this variability is unlikely to create a scenario in which a well would be misclassified with a GM issue. Values of 313 ± 15, 343 ± 10, and 425 ± 7 ppm were respectively observed for situations in which the CCD and gas were at room temperature (19 °C), when the CCD was cooled to 3 °C but the gas was at room temperature (19 °C), and when both the instrument and gas were cooled to 3 °C. As such, using the CCD at concentrations below 500 ppm may introduce some variation in CH₄ detection at low temperatures observed through sampling seasons. For example, a site may provide different results if sampled in mid-summer vs. late fall, when temperatures can reach below freezing (0 °C). Although accuracy dips at CH₄ concentrations below 500 ppm, the error is low enough that GM status would likely be unaffected due to any small shift in concentration. This means that temperature should not substantially impact the ability of a CCD to determine GM status. However, in accordance the AER Directive 20, field implemented “explosive” gas detectors, i.e., CCDs, are only required to read CH₄ concentrations above 500 ppm, so handheld CCDs should perform as required within AER guidelines (AER, 2022b).

Table 3: Expected and observed methane values with standard deviations for a handheld CCD (top) and GC (bottom-italicized) at room temperature (19 °C) and near freezing (3 °C) conditions.

Expected CH₄ Concentration (ppm)	Observed CH₄ Concentration (ppm) at Room Temperature (19 °C)	Observed CH₄ Concentration (ppm) Using Cold Device (3 °C)	Observed CH₄ Concentration (ppm) Using Cold Device & Gas (3 °C)	Standard Deviation Across Temperatures (ppm)
250	313 ± 15 <i>(198 ± 15)</i>	340 ± 10 <i>(219 ± 4)</i>	425 ± 7 <i>(224 ± 15)</i>	58 <i>(11)</i>
500	643 ± 23 <i>(464 ± 9)</i>	623 ± 33 <i>(446 ± 15)</i>	686 ± 40 <i>(420 ± 14)</i>	32 <i>(18)</i>
750	990 ± 0 <i>(717 ± 59)</i>	1000 ± 0 <i>(688 ± 14)</i>	973 ± 12 <i>(645 ± 42)</i>	13 <i>(30)</i>
1000	1267 ± 76 <i>(1030 ± 48)</i>	1283 ± 29 <i>(925 ± 28)</i>	1250 ± 0 <i>(927 ± 28)</i>	16 <i>(49)</i>
1500	1850 ± 50 <i>(1351 ± 106)</i>	1867 ± 29 <i>(1402 ± 13)</i>	1800 ± 50 <i>(1392 ± 45)</i>	34 <i>(22)</i>

3.2 Field Testing

3.2.1 Field Applications of Catalytic Combustion

Under ideal laboratory conditions and across expected field temperature ranges, the performance of the handheld CCD compared well to field GC approaches. However, minimal information is available related to the performance of the CCD device in unconstrained environments in which conditions are not always ideal for catalytic combustion. Various factors in the field may deleteriously affect the detection of CH₄ using catalytic combustion, such as humidity, dust, and the presence of acid gases. Additionally, sampling factors such as O₂ content, volume requirements, and atmospheric contamination are also possible. With such a range of potential issues, it is increasingly difficult to account for everything that may influence gas detection during an investigation. Instead of attempting to control all such variables, understanding the performance of the device on any given day may provide a more general assessment of detector effectiveness. To provide such an assessment, GC and CCD approaches were compared using the same sampling approach, with gas drawn from the same soil gas probe after a brief equilibration period.

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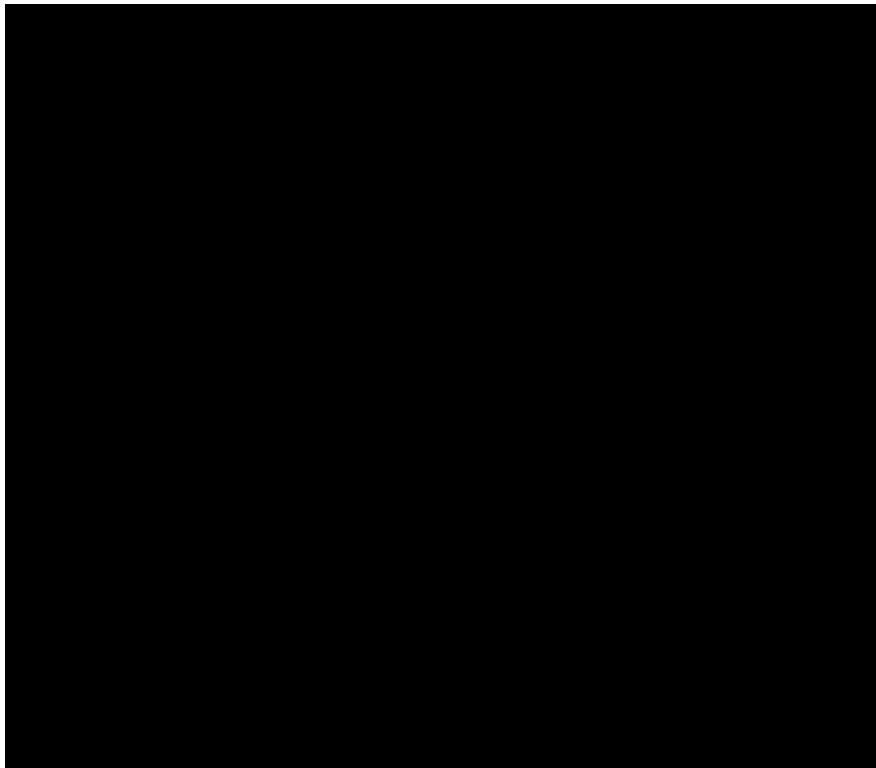


Figure 7: Relationship between observed methane concentrations drawn from samples from a soil gas probe and determined using a handheld CCD or a field gas chromatograph.

3.2.2 Factors Influencing Catalytic Combustion in the Field

Handheld CCDs are reliable in a laboratory setting, where readings are compared with known gas concentrations, with results demonstrating excellent linearity similar to that observed for GC (Figure 6a,b). However, when CCDs are used in the field with soil gas probes, linearity changes from R^2 values of 0.998 (Figure 6a) to 0.644 (Figure 7). It should be noted that comparisons made in the field were with GC measurements made on soil probes while laboratory measurements are compared to expected concentrations of gas mixtures. However, assessments made between field and laboratory measurements are comparable because GC measurements are shown to be accurate when compared to expected gas mixtures (Figure 6b). The potential sources of error are numerous and cannot all be accounted for when introducing instrumentation into an environmental setting; however, key issues addressed in this study include GC performance, O_2 requirements for catalytic combustion, and gas volume constraints related to pump rates

on CCD readings. By addressing such errors, further improvements in detector linearity may be possible in the future.

Achieving a linear relationship between field GC and CCD CH₄ detection relies on both instruments operating optimally and providing reliable values. To verify that the field GC was not responsible for the reduced linearity, discrete gas samples collected from the same sample probes were analyzed in the laboratory on a separate GC. A linear relationship was achieved between these two approaches ($R^2 = 0.972$; Figure 8), and provided evidence with respect to the reliability of field GC measurements. Minor observed differences between lab and field GC observations are likely related to sampling; field GC samples were collected directly from a soil gas probe, while lab GC samples were injected into an evacuated gas-tight sample bottle for transport to the lab and analysis, providing opportunities for atmospheric contamination. Detection quality was good using the field GC and soil probe; therefore, the handheld CCD is the most likely source of measurement error for this application.

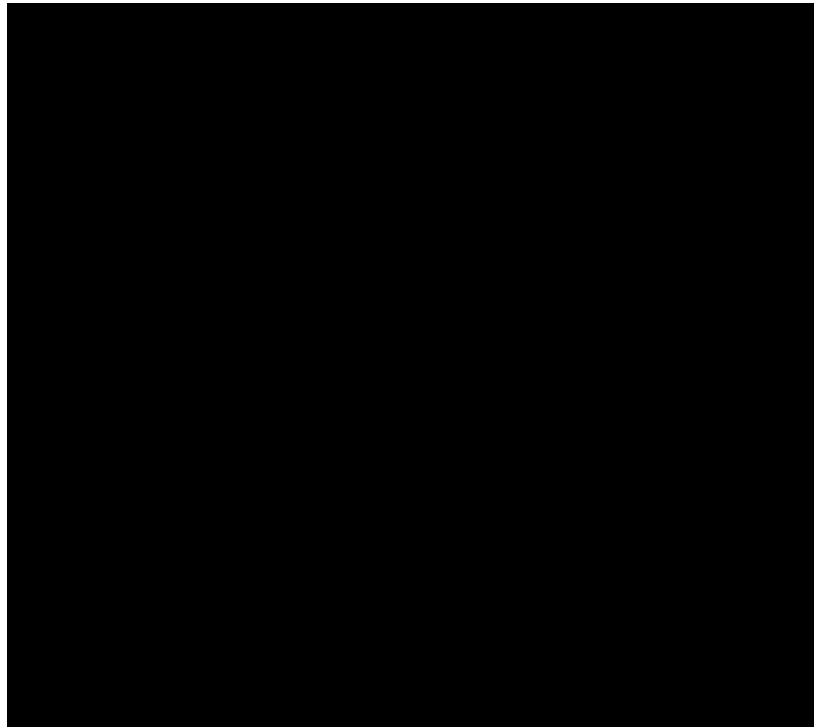


Figure 8: Observed methane concentrations from samples taken soil gas probes using field level gas chromatography versus discrete samples collected from the same probe and analyzed using gas chromatography in a laboratory setting

With respect to potential detection issues in the handheld CCD, special consideration should be given to the O₂ requirements for catalytic combustion. For catalytic combustion to occur in a handheld CCD, sample gas must contain at least 10% oxygen by volume (RKI Instruments, 2019). To address the potential of oxygen limitations in catalytic combustion, O₂ concentrations obtained from discrete gas samples, and analyzed on the laboratory GC, were compared to the ratio of CH₄ detected using field gas GC and the handheld CCD. Ideal ratios would be 1:1 with CCD measurements being equal to GC measurements; movement away from that optimal range represents measurements with the largest discrepancies (Figure 9). The relationship between oxygen concentrations and CH₄ ratios revealed no trend to suggest that any value below the 5% CH₄ threshold was due to depleted O₂ in the sample gases. However, it should be noted that O₂ concentrations obtained using the field GC only require small quantities of gas in the range of 5-10 mL, whereas the handheld CCD requires larger volumes of gas that may deplete O₂ levels throughout a reading because of low flow errors within the device. It was not possible to quantitatively account for low flow errors using the CCD instrumentation.

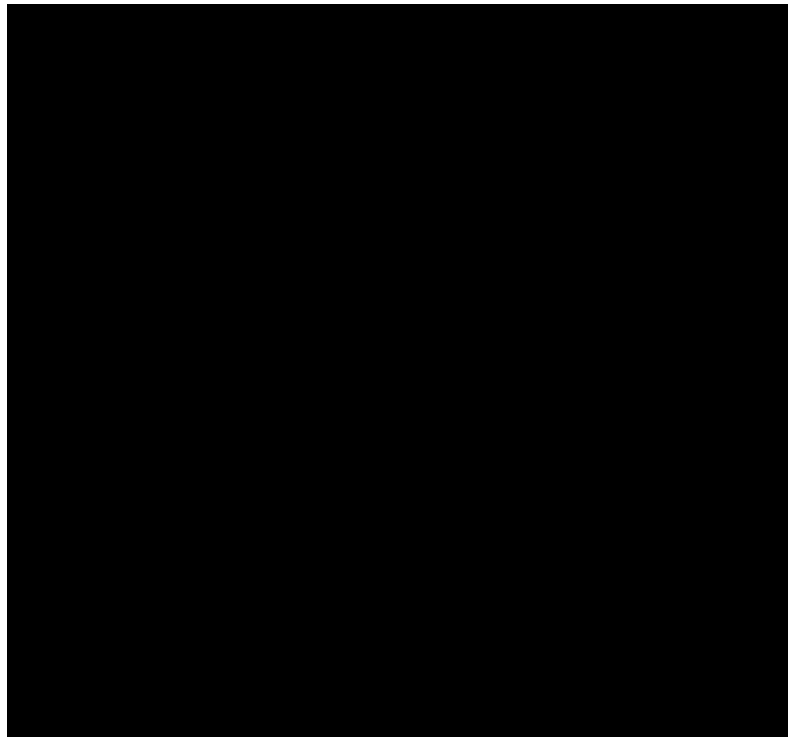


Figure 9: Oxygen concentrations of discrete laboratory samples versus the ratio of CH₄ detected in soil gas probes using a handheld CCD to the same sample analyzed using a field level gas chromatograph.

Although low flow errors could not be quantitatively assessed, the volume of gas available for analysis was likely the factor causing the different measurement results for handheld CCD gas detection vs. field GC. In a best-case scenario, the handheld CCD requires approximately 10 to 15 s of draw time for sample collection. With a draw rate of 1.0 to 1.2 L/min, an average sample would require between 167 and 300 mL of gas. Given the dimensions of soil gas probes typically used in GM investigations are approximately 30.5 cm in length and 1.3 cm in diameter, less than 40 mL of gas are available for analysis; this is much lower than the above calculated minimum volume required. Leak-sealed probes will trigger a flow error and probes with poorly sealed pathways to surface will pull gas from the surrounding soil and/or air that will contribute to atmospheric contamination of the sample. The trend in Figure 7 shows the GC measuring higher concentrations than the CCD, which supports the suggestion that dilution with air affected the gas concentrations measured and resulted in the loss of linearity observed. This observation raises concerns about the reliability of instrumentation with pump rates that exceed the volume of in-soil probes.

3.3 Methane Detection in Augured Boreholes

Gases collected from soil gas probes and analyzed by the handheld CCD returned results that reflected poor detector linearity. However, this approach features constrained volumes, requires extended equilibration times that progressively increase with larger volume probes, and can face installation difficulties in regions with highly compacted soil. Augured boreholes can be drilled to depth and quickly covered/sampled to provide an approach that overcomes many of these limitations for identifying GM status. AER Directive 20 (AER, 2022b) promotes the augured borehole approach for use in GM investigations, and therefore identifying the reliability of CH₄ concentrations obtained using this approach is of importance. To assess this subsurface borehole sampling approach, holes were augured proximal to soil gas probes used for GC and CCD analysis above, with the results from the different approaches then compared. No linear relation was found when comparing CCD measurements made on borehole samples and field GC

measurements made on soil gas probe samples ($R^2 = 0.00921$; Figure 10). The poor correlation between these results is most likely due to a trend whereby the CCD appears to, in some cases, measure higher or lower concentrations of combustible gas relative to GC measurements made on gases collected from the soil probes. Several factors likely contribute to this observation, including differences in atmospheric contamination causing dilution of sample gases, resulting in underestimations of actual soil gas concentrations, and larger open volumes in boreholes, resulting in the measurement of higher gas concentrations. Although the borehole approach does not provide accurate readings when directly compared to the soil probe approach, it can successfully measure elevated soil gas concentrations. Concentrations measured by each technique likely provide comparable relative differences; however, the absolute magnitudes of data reflecting soil gas concentrations as measured by these two techniques cannot be directly compared.

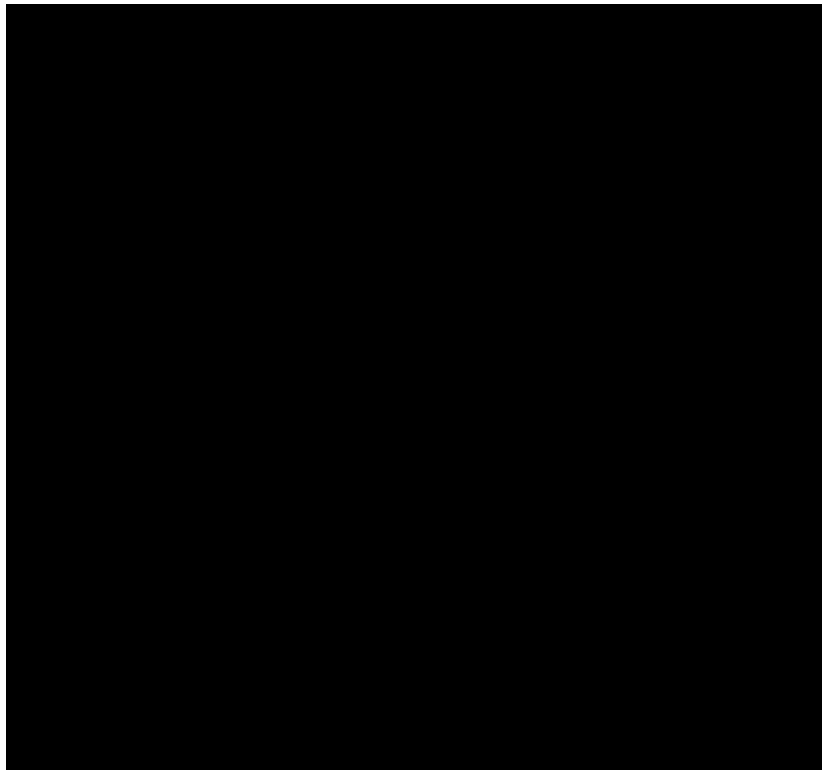


Figure 10: Observed methane concentrations measured using an augured borehole with handheld CCD versus a soil gas probe with gas chromatography detection.

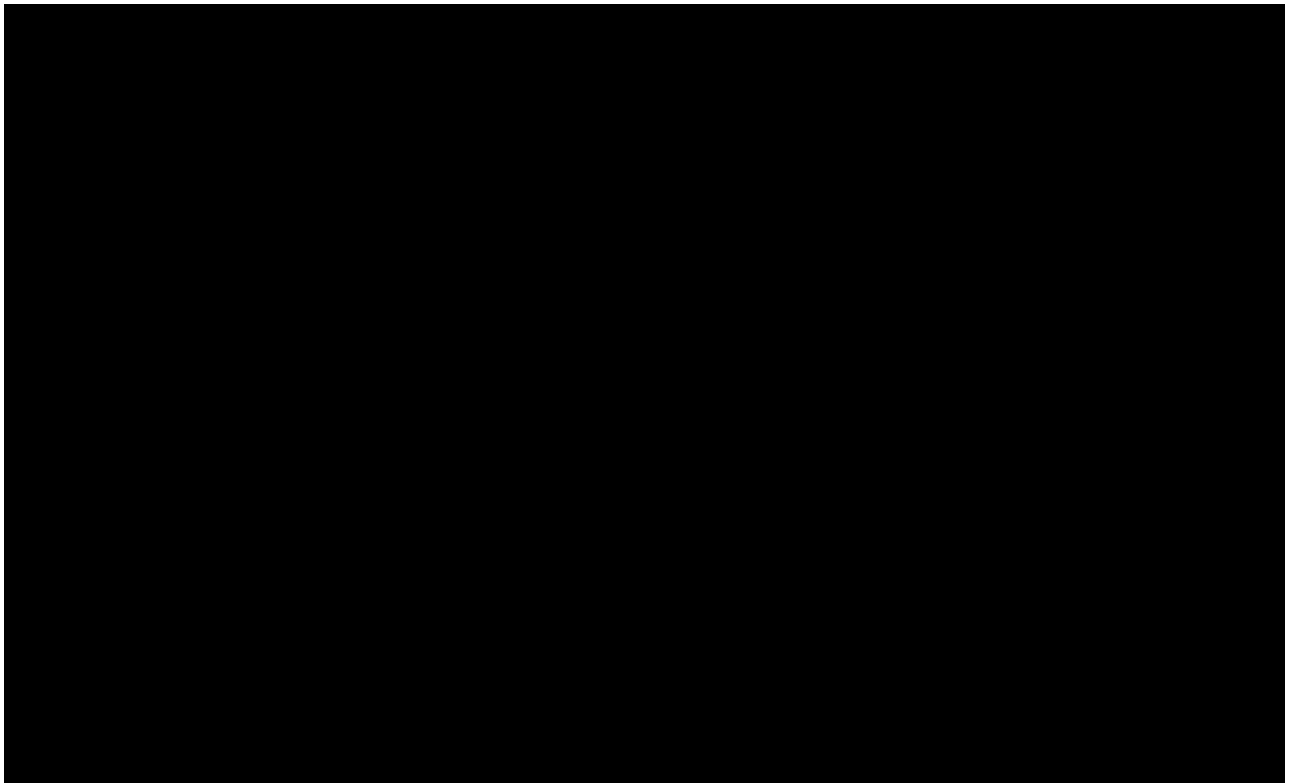


Figure 11: Various approaches to GM testing showing different results with respect to GM status

3.4.1 Effectiveness of Surface Methane Detection for Gas Migration Identification

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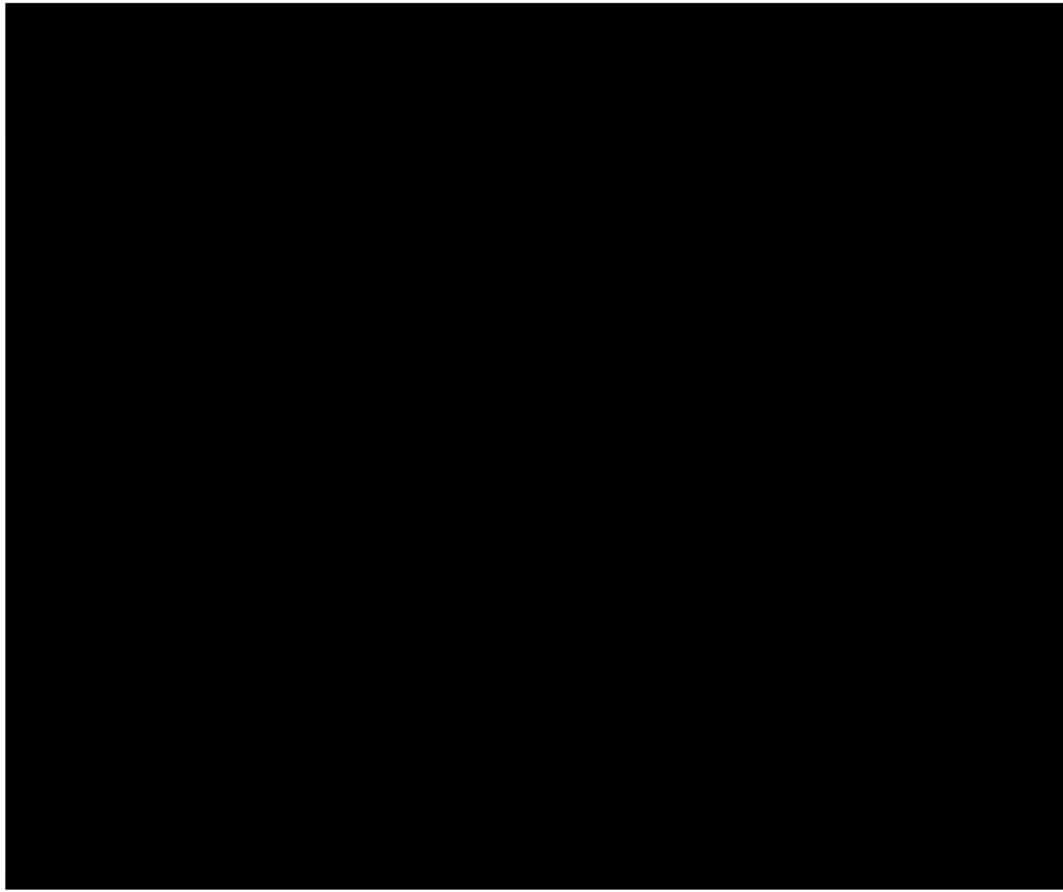
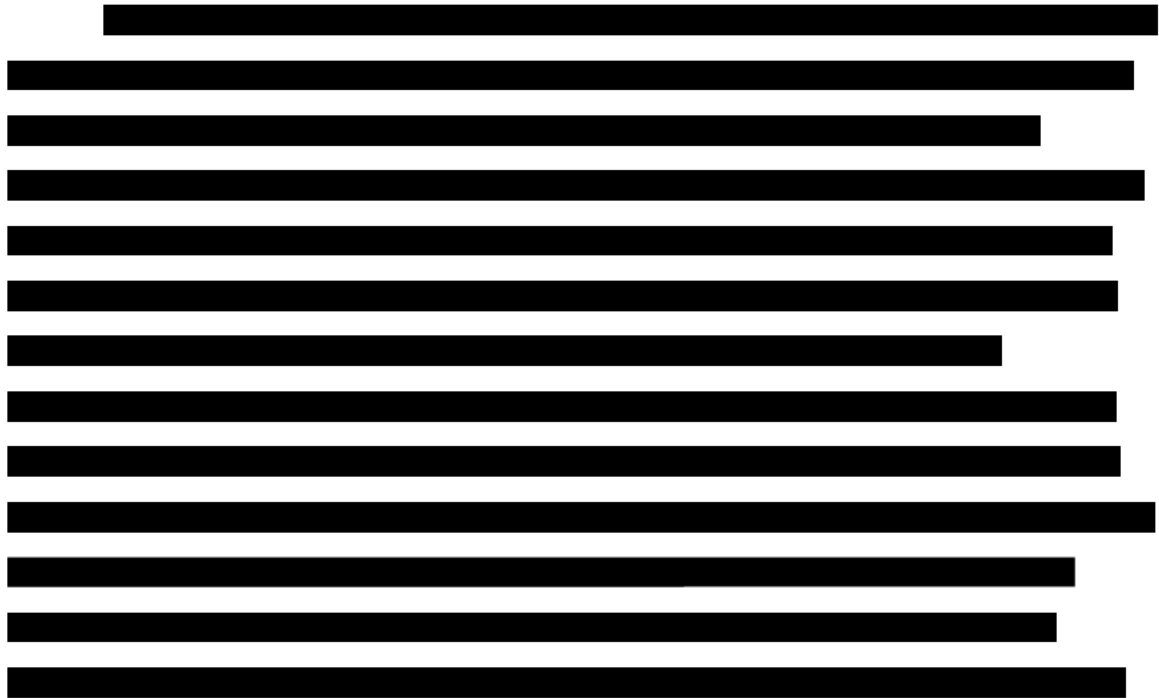


Figure 12: Effectiveness of methane detection approaches using a point-by-point comparison of data collected with and without the use of soil gas domes.



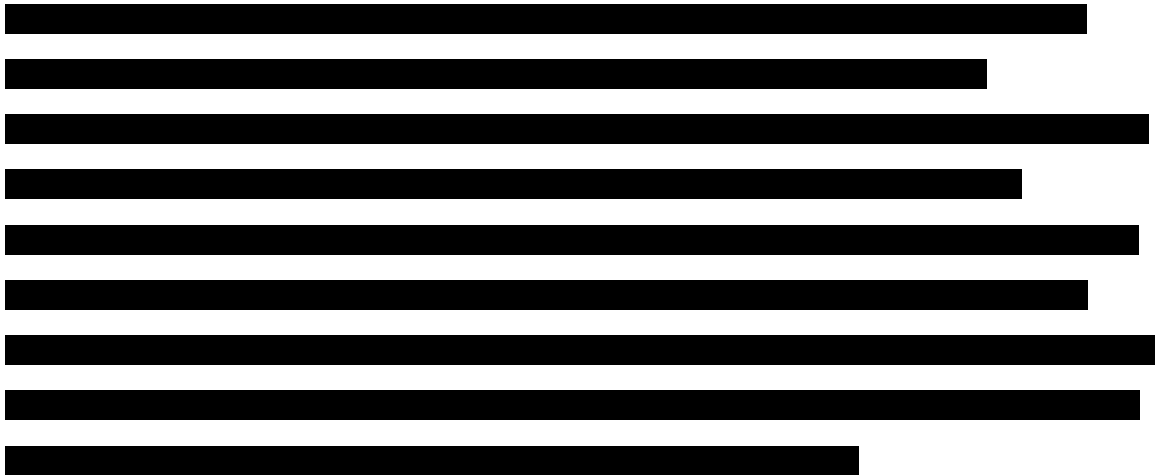
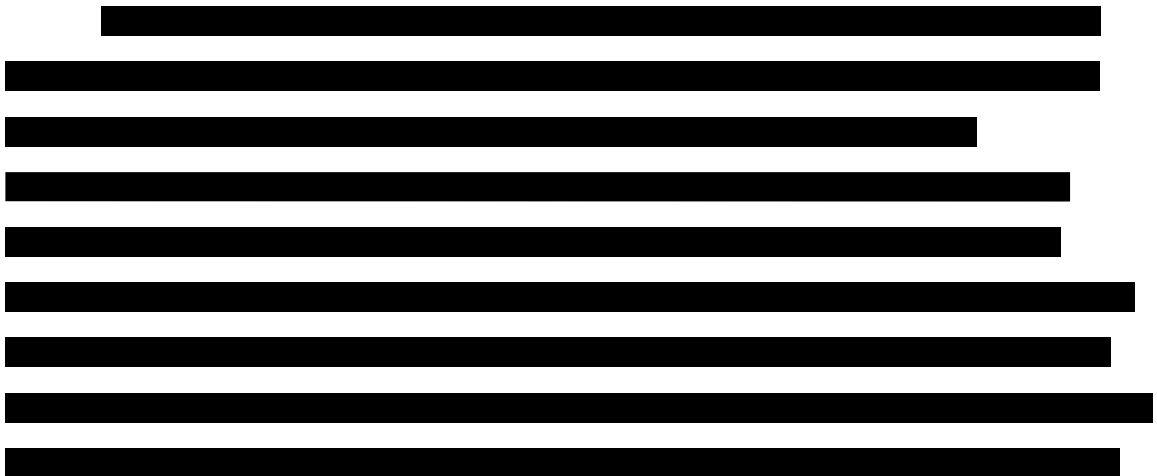


Figure 13: Percentage of measurements misclassifying a GM on a point-by-point basis for different surface/subsurface sampling techniques.



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3.4.2 Potential Sources of Error Associated with Surface Methane Detection

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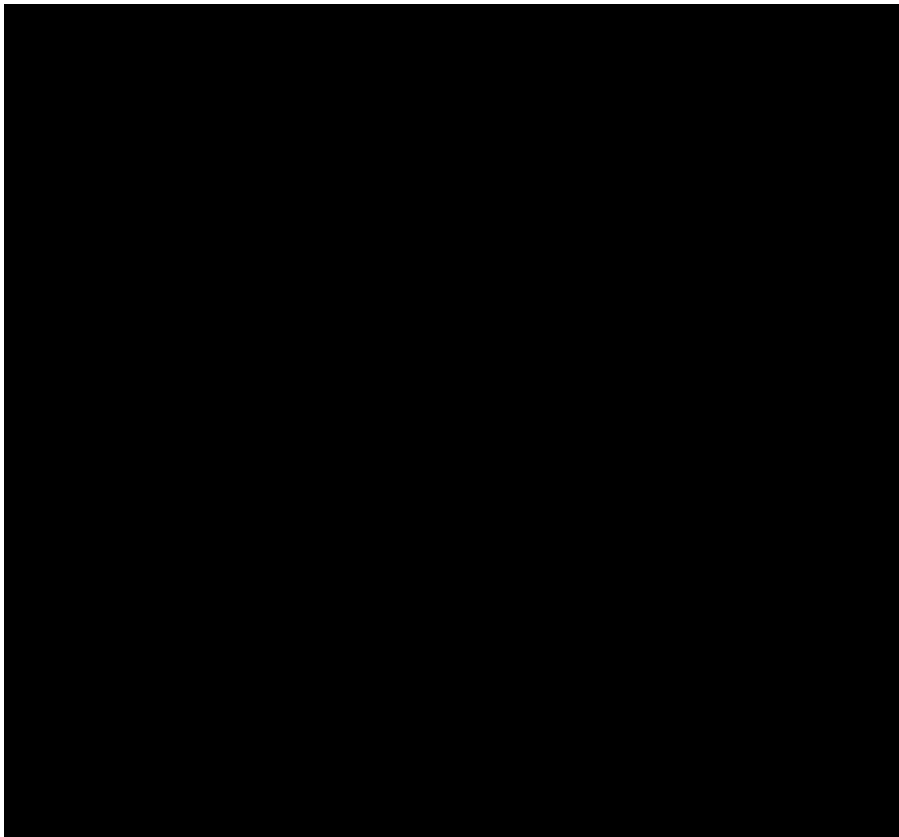
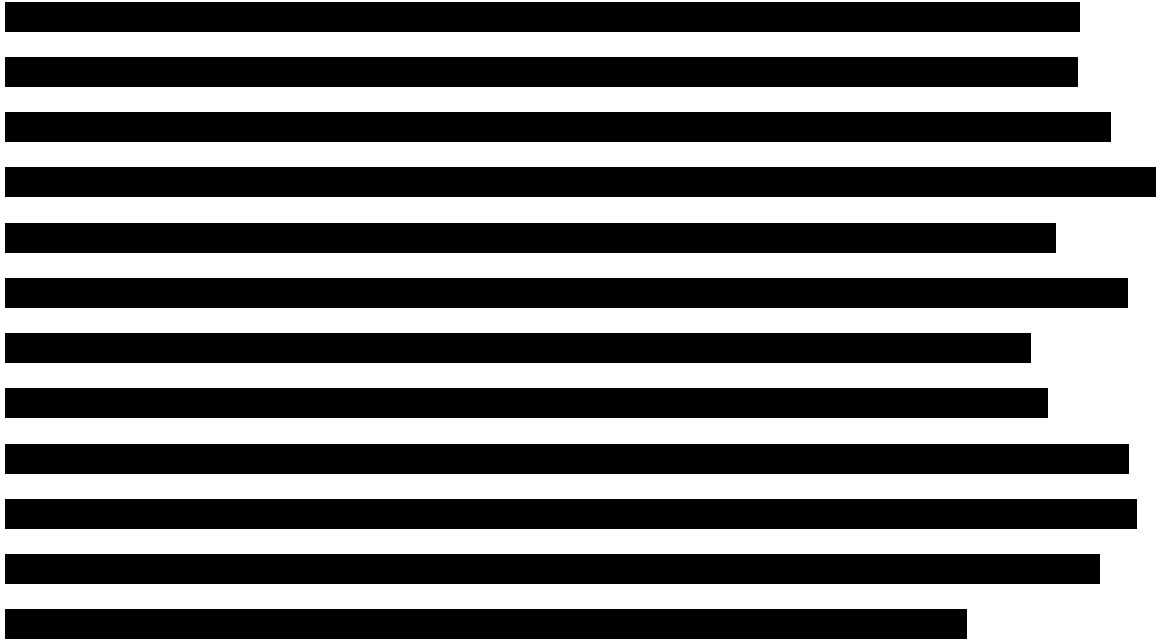


Figure 14: Observed methane concentrations detected at the surface-subsurface interface using a handheld CCD versus volumetric soil moisture content.

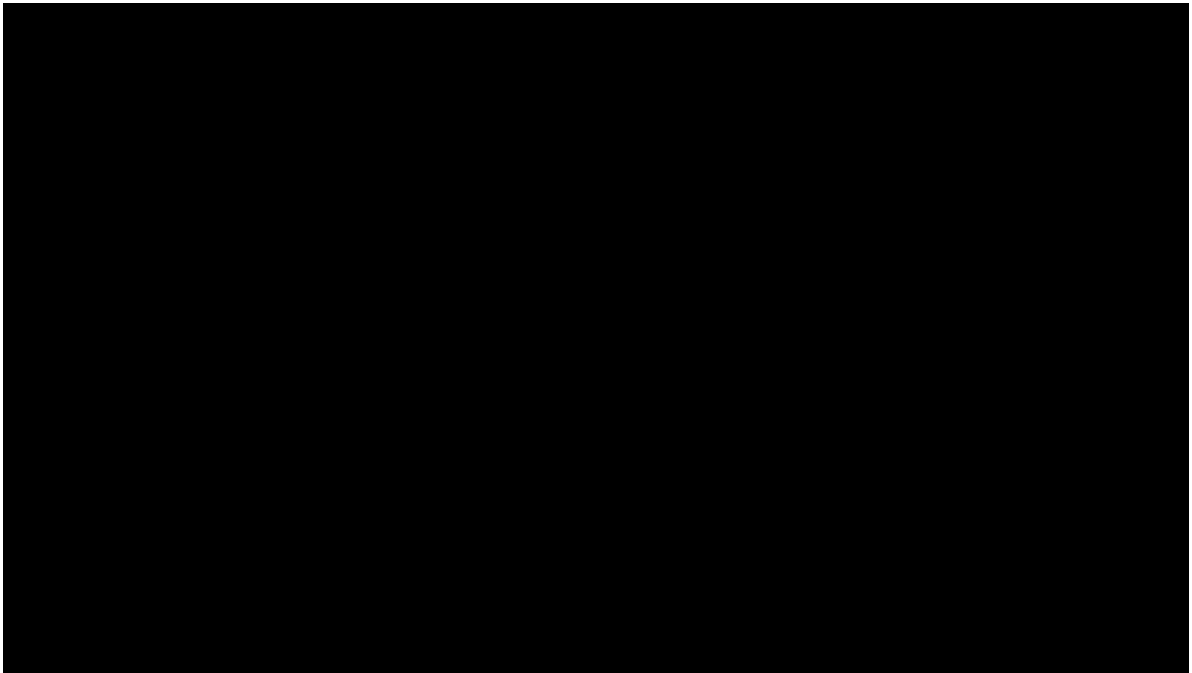


Figure 15: Observed (a) CH₄ and (b) CO₂ concentrations obtained from soil gas probes and analyzed using gas chromatography versus volumetric soil moisture content.

3.4.3 Effectiveness of Soil Gas Probes and CCDs for Gas Migration Identification

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3.4.4 Effectiveness of Augured Boreholes for Gas Migration Identification

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Table 4: Methane detection using various GM testing approaches at site 1-sample event 1.

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Table 5: Methane detection using various GM testing approaches at site 1-event 2 day 1.

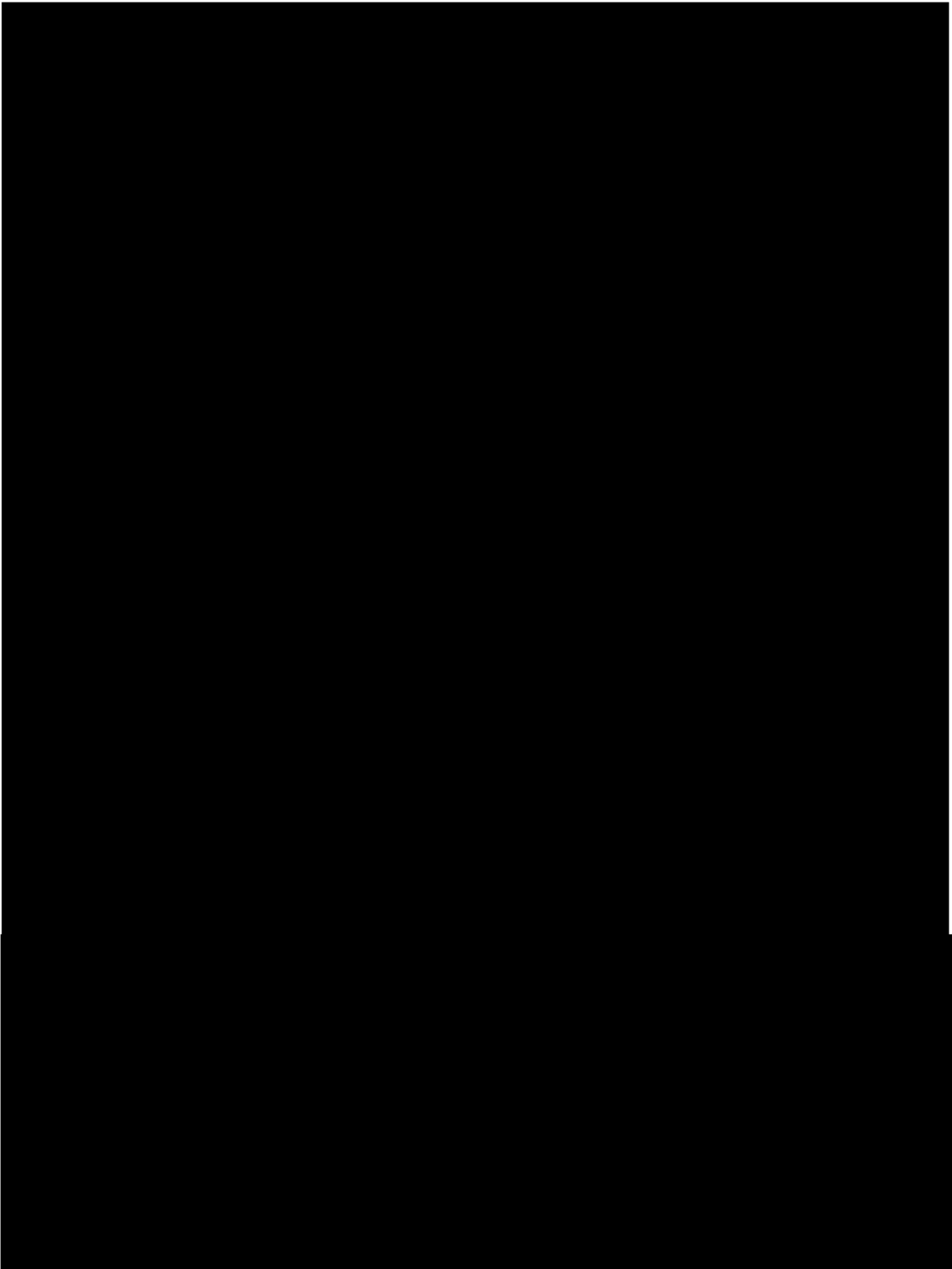
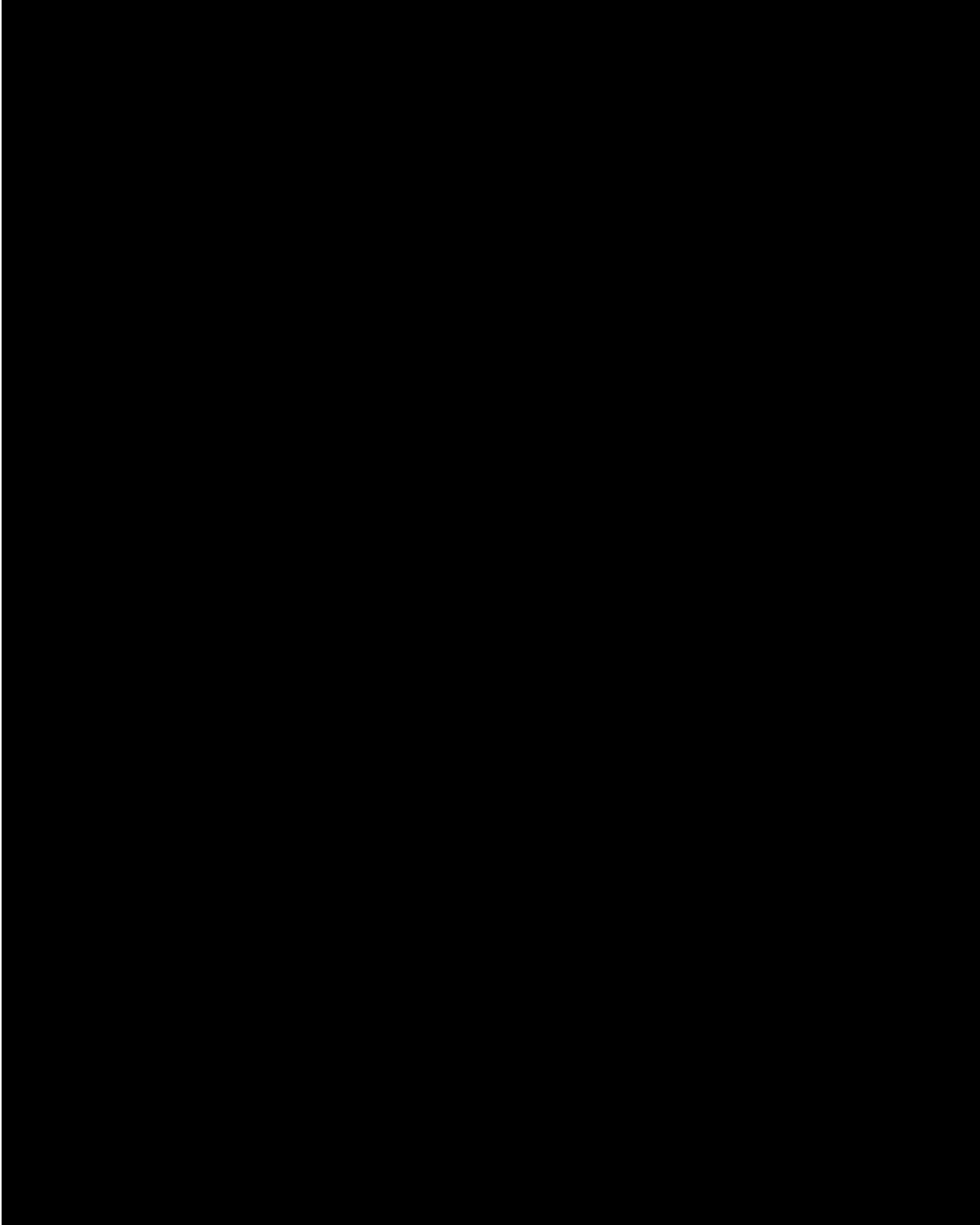
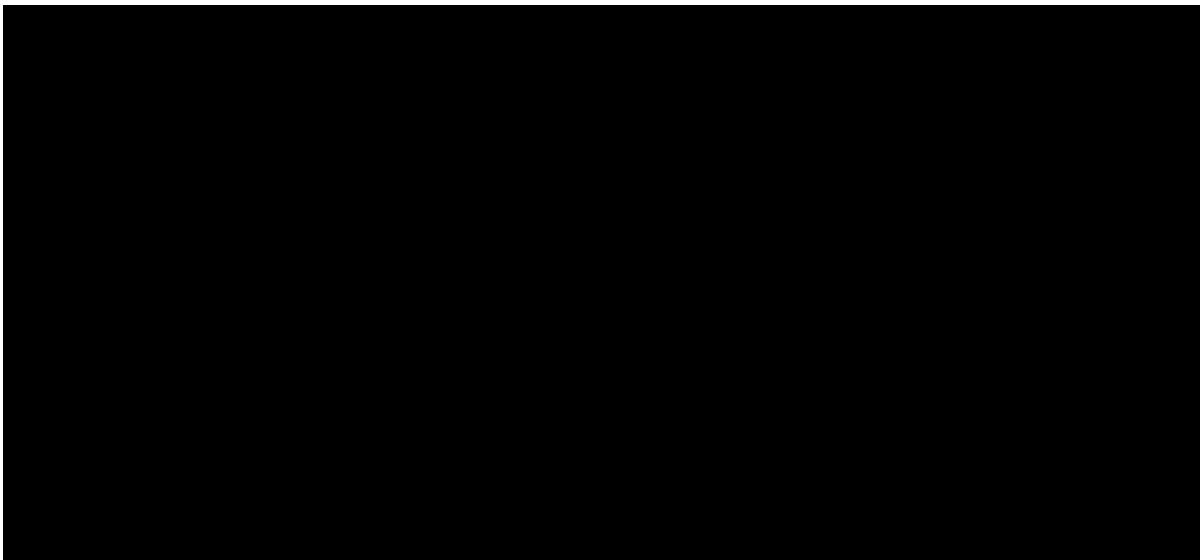


Table 7: Methane detection using various GM testing approaches at baseline control site.





3.5 Recommendations of Use for CCDs in Gas Migration Testing

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3.6 Considerations for Future Gas Migration Procedures

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[REDACTED]

CHAPTER IV

CONCLUSIONS

[REDACTED]

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REFERENCES

- Alberta Energy Regulator. 2014. Directive 79: Surface Development in Proximity to Abandoned Wells. Energy Conservation Board. Calgary Alberta.
- Alberta Energy Regulator. 2022a. Directive 17: Measurement Requirements for Oil and Gas Operations. Energy Conservation Board. Calgary, Alberta.
- Alberta Energy Regulator. 2022b. Directive 20: Well abandonment. Energy Conservation Board. Calgary, Alberta.
- Alberta Energy Regulator. 2022c. Directive 60: Upstream Petroleum Industry Flaring, Incinerating, and Venting. Energy Conservation Board. Calgary, Alberta.
- Alberta Energy Regulator. 2022d. Directive 87: Well Integrity Management. Energy Conservation Board. Calgary Alberta.
- Province of Alberta. 2021. Pipeline Act Revised Statutes of Alberta 2000 Chapter P15. June 19, 2021. https://www.qp.alberta.ca/1266.cfm?page=p15.cfm&leg_type=Acts&isbncln=9780779827855.
- Aldhafeeri, T., Tran, M., Vrolyk, R., Pope, M., Fowler, M. 2020. A review of methane gas detection sensors: recent developments and future perspectives. *Inventions* 5(3), 28.
- Arya, L.M., Paris, J.F. 1981. A physicoempirical model to predict the soil moisture characteristic from particle-size distribution and bulk density data. *Soil Science Society of America Journal* 45, 1023–1030.
- B., W. 1918. Diurnal variation of atmospheric pressure. *Nature* 101, 253–254. DOI: <https://doi.org/10.1038/101253b0>.
- Bachu, S. 2017. Analysis of gas leakage occurrence along wells in Alberta, Canada, from a GHG perspective – Gas migration outside well casing. *Int. J. Greenh. Gas Control* 61, 146–154.

- Baldassare, F.J., McCaffrey, M.A., Harper, J.A. 2014. A geochemical context for stray gas investigations in the northern Appalachian Basin: Implications of analyses of natural gases from Neogene-through Devonian-age strata. *AAPG Bull.* 98, 341-372.
- Benavente, D., Pla, C. 2018. Effect of pore structure and moisture content on gas diffusion and permeability in porous building stones. *Mater Struct* 51, 21.
- Cahill, A., et al. 2017. Mobility and persistence of methane in groundwater in a controlled release field experiment. *Nat Geosci.* 10, 289-294.
- Canadian Environmental Protection Agency. 2018. Regulations Respecting Reduction in the Release of Methane and Certain Volatile Organic Compounds (Upstream Oil and Gas Sector); SOR/2018-66; Gatineau, QC.
- Canadian Society of Soil Science. 2020. Soils of Canada. July 13th, 2022.
soilsofcanada.ca.
- Chapuis, R.P. 2012. Predicting the saturated hydraulic conductivity of soils: a review. *Bull Eng Geol Environ* 71, 401-434.
- Civeira, G. 2019. Introductory Chapter: Soil Moisture. In (Ed.), Soil Moisture. IntechOpen. DOI: <https://doi.org/10.5772/intechopen.83603>
- Dean, J.F., Middelburg, J.J., Röckmann, T., Aerts, R., Blauw, L.G., Egger, M., et al. (2018). Methane feedbacks to the global climate system in a warmer world. *Reviews of Geophysics* 56, 207–250. 3.
- Dolzyk, K., Chmielewska, I. 2014. Predicting the coefficient of permeability of non-plastic soils. *Soil Mech Found Eng* 51, 213–218. DOI: <https://doi.org/10.1007/s11204-014-9279-3>.
- Environment Canada. 2014. Canada's Emissions Trends; En81-18/2014E-PDF; Gatineau, QC.
- Environment and Climate Change Canada. 2016. Canada's mid-century longterm low-greenhouse gas development strategy. Gatineau, Quebec.

- Environment and Climate Change Canada. 2021. Canadian Environmental Sustainability Indicators: Greenhouse gas emissions. *April 10, 2021*.
www.canada.ca/en/environment-climate-change/services/environmental-indicators/greenhouse-gasemissions.html.
- Erno, B., Schmitz, R. 1996. Measurements of soil gas migration around oil and gas wells in the Lloydminster Area. *J. Can. Pet. Technol.* 35.
- Etnyre, L.M. 1989. Porosity and saturation. In: Finding Oil and Gas from Well Logs. Springer, Boston, MA. DOI: https://doi.org/10.1007/978-1-4757-5230-4_2
- Forde, O.N., et al. 2018. Vadose zone gas migration and surface effluxes following a controlled natural gas release into an unconfined shallow aquifer. *Vadose Zone J.* DOI: <https://doi.org/10.2136/vzj2018.02.0033>.
- Forde, O.N., Cahill, A.G., Beckie, R.D., et al. 2019. Barometric-pumping controls fugitive gas emissions from a vadose zone natural gas release. *Sci Rep* 9, 14080. DOI: <https://doi.org/10.1038/s41598-019-50426-3>
- Gao, B., Mitton, M.K., Bell, C., Zimmerle, D., Chamindu Deepagoda, T.K.K., Hecobian, A., Smits, K.M. 2021. Study of methane migration in the shallow subsurface from a gas pipe leak. *Elementa: Science of the Anthropocene* 9(1).
DOI: <https://doi.org/10.1525/elementa.2021.00008>.
- Government of Alberta. 2018. Climate Leadership Plan: Implementation Plan 2018-19. Alberta Climate Change Office, Calgary, AB.
- Government of Canada. 2020a. Crude Oil Industry Overview. June 22, 2022.
<https://www.nrcan.gc.ca/our-natural-resources/energy-sources-distribution/clean-fossil-fuels/crude-oil-industry-overview/18078>.
- Government of Canada. 2020b. Everything you need to know about multi-gas detectors! June 22, 2022. <https://www.tc.gc.ca/eng/canutec/articles-mgas-329.html>.

- GOW-MAC Instrument Co. 2018. Operating Manual Models A16-0001, A16-0002 Portable Blender for Gas Standards. May 21, 2022. http://www.gow-mac.com/wp-content/uploads/2020/01/Blender-_R3.pdf.
- Heath Consultants Incorporated. 2019. DP-IR User's Manual. June 26, 2022. <https://heathus.com/assets/uploads/DP-IRManualRevN.pdf>.
- ICF International. 2015. Economic Analysis of Methane Emission Reduction Opportunities in the Canadian Oil and Natural Gas Industries. Prepared for Environmental Defence Fund. June 21, 2022. <https://www.pembina.org/reports/edf-icf-methane-opportunities.pdf>.
- Kelly, W.R., et al. 1985. The effects of a gas-well blow-out on groundwater chemistry. *Environ. Geol. Water Sci.* 7, 205-213.
- Kemfert, C. and Schill, W. 2009. Methane: A Neglected Greenhouse Gas. *Deutsches Institut für Wirtschaftsforschung (DIW), Berlin*, 5 (32), 218-223.
- Kiran, R., et al. 2017. Identification and evaluation of well integrity and causes of failure of well integrity barriers (A review). *J Nat Gas Sci Eng* 45, 511–526.
- Koorevaar, P., Menelik, G., Dirksen, C. (Eds.) 1983. Gas transport in soil. *Developments in Soil Science* 13, 183-192. DOI: [https://doi.org/10.1016/S0166-2481\(08\)70053-9](https://doi.org/10.1016/S0166-2481(08)70053-9).
- Kruczek, B. 2016. Diffusive flow. In: Drioli, E., Giorno, L. (Eds.), *Encyclopedia of Membranes*. Springer, Berlin, Heidelberg. DOI: https://doi.org/10.1007/978-3-662-44324-8_1996.
- Li, B., Wang, L., Kaseke, K.F., Li, L., Seely, M.K. 2016. The impact of rainfall on soil moisture dynamics in a foggy desert. *PLoS One*. 11(10). DOI: 10.1371/journal.pone.0164982.
- Massmann, J., Farrier, D.F. 1992. Effects of atmospheric pressures on gas transport in the vadose zone. *Water Resour Res* 28, 777–791.
- Mayer, B., et al. 2013. Tracing the movement and the fate of injected CO₂ monitoring and storage project (Saskatchewan, Canada) using carbon isotope ratios. *Int J Greenh Gas* 16, 177-184.

- Niya, S.M.R., Selvadurai, A.P.S. 2018. A statistical correlation between permeability, porosity, tortuosity and conductance. *Transp Porous Med* 121, 741–752. DOI: <https://doi.org/10.1007/s11242-017-0983-0>.
- Osborne, S.G., Vengosh, A., Warner, N.R., Jackson, R.B. 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *PNAS* 20, 8172-8176.
- Phillips, F.M., Castro, M.C. 2014. 7.11 - Groundwater dating and residence-time measurements. *Treatise on Geochemistry*, 7, 361-400. DOI: <https://doi.org/10.1016/B978-0-08-095975-7.00513-1>.
- RKI Instruments. 2019. Eagle 2 Operator’s Manual. June 23, 2022. <https://www.rkiinstruments.com/pdf/71-0154RK.pdf>.
- Rostron, B., Arkadakskiy, S. 2014. Fingerprinting “stray” formation fluids associated with hydrocarbon exploration and production. *Elements* 10, 285-290.
- Rowe, D., Muehlenbachs, A. 1999. Low-temperature thermal generation of hydrocarbon gases in shallow shales. *Nature* 398, 61-63.
- Seely, G.E., Falta, R.W., Hunt, J.R. 1994. Buoyant advection of gases in unsaturated soil. *J Environ Eng* 120(5), 1230-1247. DOI:10.1061/(ASCE)0733-9372(1994)120:5(1230)
- Smith, I. 2006. *Smith's Elements of Soil Mechanics*, Blackwell Publishing, Oxford, UK.
- Szatkowski, B., Whittaker, S., Johnston, B. 2002. Identifying the source of migrating gases in surface casing vents and soils using stable carbon isotopes, Golden Lake Pool, West-central Saskatchewan. *Sum Invest* 1, 118-125.
- Topp, E., Pattey, E. 1997. Soils as sources and sinks for atmospheric methane. *Can J Soil Sci* 77(2), 167-177. DOI: <https://doi.org/10.4141/S96-107>
- VanLoon, G.W., Duffy, S.J. 2005. *Environmental chemistry: A global perspective*. Oxford: Oxford University Press.

- Vidic, R.D., Brantley, S.L., Vandenbossche, J.M., Yoxtheimer, D., Abad, J.D. 2013. Impact of shale gas development on regional water quality. *Science* 340, 1235009.
- Wang, Y., Tong, M.M., Zhang, D., Gao, Z. 2011. Improving the performance of catalytic combustion type methane gas sensors using nanostructure elements doped with rare Earth cocatalysts. *Sensors (Basel)* 1, 19–31.
- Whalen, S.C., Reeburgh, W.S., Sandbeck, K.A. 1990. Rapid methane oxidation in a landfill cover soil. *App Environ Microbiol* 56, 3405–3411.
- Williams, P.J., Regehr, A., Kang, M. 2021. Methane emissions from abandoned oil and gas wells in Canada and the United States. *Environ Sci Technol* 55, 1, 563–570.

VITA AUCTORIS

NAME: Matthew Day

PLACE OF BIRTH: London, ON

YEAR OF BIRTH: 1996

EDUCATION: John Paul II Catholic Secondary School, London,
ON, 2014

University of Windsor, B.Sc., Windsor, ON, 2020

University of Windsor, M.Sc., Windsor, ON, 2022