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Gas Migration Testing at Abandoned Well Sites in Western Canada

By

Kelsey Lauren Friesen

A Thesis
Submitted to the Faculty of Graduate Studies
through the Department of Chemistry and Biochemistry
in Partial Fulfillment of the Requirements for
the Degree of Master of Science
at the University of Windsor

Windsor, Ontario, Canada

2020

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Gas Migration Testing at Abandoned Well Sites in Western Canada

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September 8th, 2020

DECLARATION OF ORIGINALITY

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ABSTRACT

Fugitive releases from natural gas wells are a persistent issue in the oil and gas sector and comprises 27% of Canada's greenhouse gas emissions. Natural gas within this sector accounts for 44% of Canada's methane releases and 70% of Alberta's. Releases from wells are documented; however, knowledge gaps persist for abandoned assets. When fugitive gases are suspected, regulatory standards require gas migration testing. This thesis presents the beginnings of developing 'best practices' in testing recommendations to better estimate emissions from abandoned wells. Testing requires detection of stray gases utilizing a worker-safety portable handheld multi-gas monitor; however, our work shows this monitor has limited application in gas migration testing. Portable monitors are equipped with non-specific, catalytic combustion sensors that underestimate methane concentrations in the subsurface. To circumvent misleading results, we suggest reporting oxygen levels for subsurface gases or the use of more sophisticated detectors. Additionally, work enclosed addresses single-sample, or sample-to-sample, risk assessments for gas migration testing. A brief commentary on previous testing at an abandoned well site in Western Canada reveals how this approach often produces insufficient evidence of stray gases. In applying a multivariate risk assessment method, using principal component analysis and K-means clustering, we showed sample sizes >20 for reporting gas compositions and >10 for stable isotopes will accurately detect stray gases at an abandoned well. Best practices highlighted in each study can easily be integrated into testing recommendations that will assist Canada in reducing emissions by 45% in 2025.

DEDICATION

I would like to dedicate this thesis to my parents:

Gordon and Judith Friesen

And to my siblings:

Amy, Aaron, Gunnar, and Addison Suderman

Ashley Friesen

Allison and Jason Zacharias

Kaylee and Kyle Bergen

Your support and care are constants I can rely on.

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LIST OF ABBREVIATIONS/SYMBOLS

AER	Alberta energy regulator
AGM	Active gas migration
ATP	Adenosine triphosphate
ANOVA	Analysis of covariance
BDL	Below detection limit
CC	Catalytic combustion
CCD	Catalytic combustion detector
FG(s)	Fugitive gas(es)
FID	Flame ionization detector
GC	Gas Chromatograph
GHG(s)	Greenhouse gas(es)
GIS	Geographic information systems
GM	Gas migration
GPS	Global positioning system
GWP	Global warming potential
IR	Infrared
KIE	Kinetic Isotope Effect
LAOGMT	Lloydminster Area Operations Group Gas Migration Team
LEL	Lower explosive limit
NM	Not measured
NRCan	Natural Resources Canada
ODL	Over detection limit
O&G	Oil and gas
PAM	Partition around medoids
PCA	Principal component analysis
PC(s)	Principal component(s)
R&D	Research and development
SCV	Surface casing vent
SCVF	Surface casing vent flow
SVD	Singular value decomposition

TCD	Thermal conductivity detector
VMSOW	Vienna Mean Standard Ocean Water
VPDB	Vienna Pee Dee Belemnite
δ	Isotope ratio

CHAPTER 1

INTRODUCTION

1.1. Greenhouse gases in the oil and gas sector

Quantifying the potential warming effect of greenhouse gases (GHGs) on the Earth's atmosphere is based on the fundamental photochemical reactions of gases that result in the absorption of light in the infrared (IR) region.¹ The greater the capacity of a gas to absorb light energy, the more it can subsequently heat the atmosphere.^{1,2} Global warming potential (GWP) is a metric that captures this property of absorptivity and scales it to the atmospheric concentration of the gas.¹ GWP values are benchmarked to 1 ton of carbon dioxide (CO₂) and warming potential is projected over a span of 100 years.^{1,2} The disadvantage of using a long time-frame is the failure to capture the residence time of a gas. For example, methane (CH₄) has a residence time of 12 years in the atmosphere; its GWP is 28 times greater than CO₂ over a 100-year timeframe but 84 over a 20-year timeframe.² An important consideration for GWP calculations is the chemical cycle of a GHG within the biogeochemical cycle, which includes all abiotic and biotic compartments of the environment.² Accounting for additional pathways related to a GHG can increase its GWP. The major depletion route or sink of the CH₄ cycle is reactivity with water vapour and oxidation to CO₂, resulting in an increase in another GHG in the atmosphere¹ through a positive feedback loop^{1,2}. Accounting for this process means the GWP of CH₄ is 86 times greater than CO₂ over a 20-year timeframe.² Due to its potency, Canada's action plan specifically targets CH₄ and aims to reduce this GHG by 40–45% by the year 2025, relative to 2012 emissions, starting with the oil and gas (O&G) sector.³

Canada's emissions constitute 1.6% of total GHGs (CO₂ equivalent) emitted into the atmosphere, making it the ninth-largest contributor by country.^{3,4} Its O&G sector emits more GHGs to the atmosphere (27%; CO₂ equivalent) than any other sector, with a quarter sourced to natural gas.^{3,5,6,7} Natural gas is primarily composed of CH₄, with the O&G sector consequently contributing 44% of Canada's CH₄ emissions.³

With over 300,000 wells, the Province of Alberta accounts for the majority (65%) of Canada's natural gas energy projects.^{8,9} Emissions from these projects total over 70% of the province's CH₄.^{5,6} Hence, the Government of Alberta has committed alongside Canada to reduce CH₄ emissions by in this sector.¹⁰ Canada and the Alberta Energy Regulator (AER) have identified O&G infrastructure as the main source of fugitive gases (FGs), which include practiced/operational and unintended releases.^{3,7} From 1990 to 2017, venting and flaring practices from surface casings of natural gas wellheads roughly doubled.⁵ Regulatory mechanisms have since been in place to reduce these practices, but FGs from unintended releases continue.^{5,6} Contributions from unintended sources were estimated by Environment and Climate Change Canada in 2017 to comprise a small portion (7-9%) of Canada's emissions.⁶ In 2016, Natural Resources Canada (NRCan) assessed 440,000 wells drilled in the upstream (crude oil and natural gas) sector in Alberta and found unintended releases were only reported for 5% of these wells, with the majority (97%) not requiring immediate remediation.⁷ Independent studies provide similar estimates, reporting 4.5–4.6% of wells drilled from 1910 to 2004 released unintended FGs and only 0.5% of wells in Alberta reported as drilled and abandoned with an integrity issue.^{7,11} A 2011 study from the US reported 5–8% of CH₄ emissions from Pennsylvania are sourced to

unintended FGs from abandoned wells.¹² Abandoned wells in Alberta appear to have higher rates of FG emissions, with the occurrence of release issues observed at 6% or 14% of wells, which depends on the number of abandoned wells monitored in this sector.^{11,12,13} Percent estimates rely on industry reporting from Alberta regulators that submit documentation to the AER and update open databases for researcher access. Reporting of emissions and defining FG sources are highlighted as areas in need of improvement by NRCAN, AER, and researchers alike.^{7,11,12,13}

1.2. Fugitive gases from natural gas wells

Significant opportunities reside within the natural gas sector for Canada to achieve its climate goal of reducing CH₄ emissions.⁷ With practices releases undergoing regulatory reform in 2017, unintended FGs provide the next focal point for regulatory reform by governing bodies.⁵ Advancements in drilling and construction technology in Alberta have been key to decreasing FGs from this sector.^{11,12} Extensive studies provide significant insight into practices that propagate FG issues throughout the sector.^{11-14,16,17} Two main types of unintended releases from natural gas wells are identified: surface casing vent flows (SCVFs) and gas migration (GM).^{14,15} SCVFs are fugitive releases originating from failure within the wellbore infrastructure, whereas GM occurs when FGs penetrate the surrounding soil environment (Figure 1).^{15,16,18}

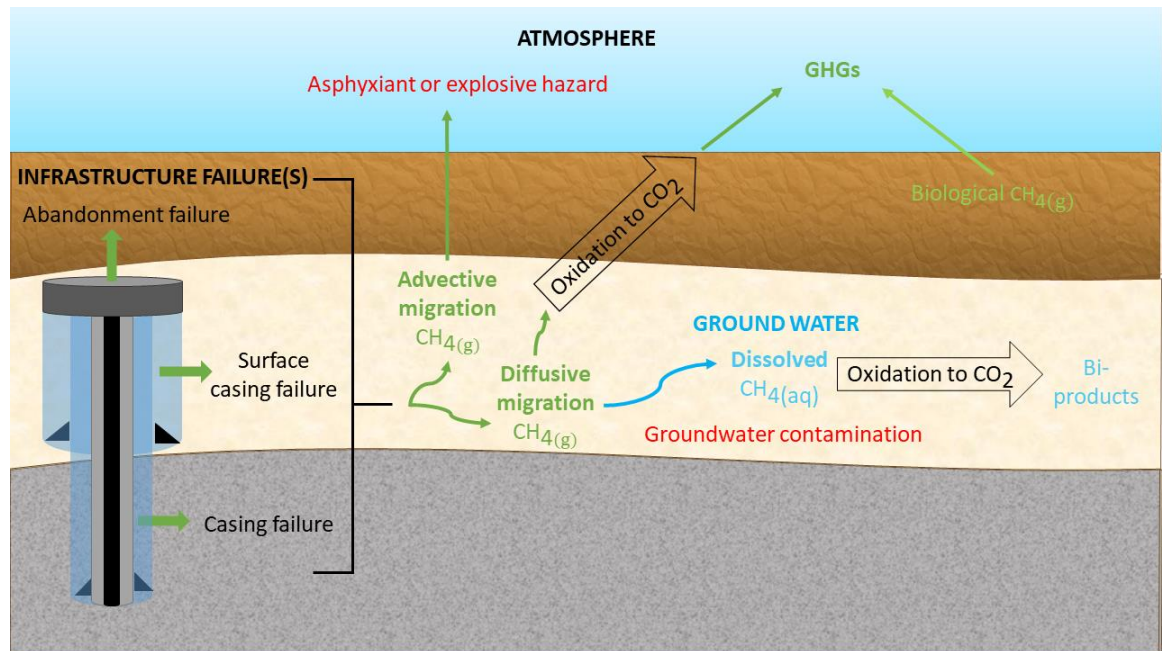


Figure 1.1 Gas migration pathways (not to scale).¹⁵

The surface casing is the outermost cement barrier of the wellbore that protects potable aquifers and separates gases from the subsurface or soil environment.¹⁵ SCVF is caused by gases collecting in the surface casing from production tubing and subsequently being released directly into the atmosphere from the wellhead.^{7,14,15} These releases are propagated by seal cracking/fracturing in the cement casings surrounding the production tubing.^{7,15} The quality of the cement bond and corrosion over time are common factors related to SCVF releases.^{11,12,14,15} Detection of SCVF is completed by measuring the rate of gas flow from the SCV and is the least complex type of release to characterize.¹⁷⁻¹⁹ Regulations classify stabilized vent flows ≥ 300 m³/d as a serious concern that requires immediate attention.^{19,20} In contrast, the lack of a stabilized flow may indicate a GM issue, which is an uncontrolled and unintended release of natural gas from the wellbore into the soil.¹⁶ GM issues result from infrastructure failures similar to those indicated for SCVF releases.^{7,11-15,17,18} When FGs make contact with the adjacent formation, they can migrate in various

directions prior to reaching the surface of the well site (Figure 1.1).¹⁵ A study on British Columbia energy wells identified the possible types of conventional active gas migration (AGM) pathways, where CH₄ in the subsurface can either migrate in a free-phase, gaseous state or dissolved in a liquid state.¹⁵ Free-phase CH₄ can migrate either by advection (due to a pressure gradient) or diffusion (due to a concentration gradient movement) through overlying formations.^{15,21} Pathways that commonly interfere and complicate the migration of gases are CH₄ oxidation and the presence of natural biological (biogenic) CH₄.^{15,18,22–25} GM pathways can be mitigated by methanotrophic bacteria that consume CH₄ from natural gas in the soil as an energy source.^{22–24} FGs can be biologically converted into CO₂ before reaching the surface of a well site, thus masking any surface measurements of AGM.^{15,22} Conversely, natural biogenic CH₄ is produced by degradation processes in the soil by methanogens in low oxygenated soils.^{24–26} Methanogens can enhance a GM pathway or produce gases on a scale that can be mistaken for AGM.²⁵ Pathway identification for GM-type releases has been extensively researched due to the potential hazards that may occur with the accumulation of FGs.^{11–15,21} A serious GM is indicated when natural gas seepage is detected at the surface surrounding the well centre, contaminates potable groundwater aquifers, or is a potential explosive and/or asphyxiant hazard.^{19,20} The well must be remediated immediately if one of these events or hazards is detected.²⁰

Infrastructure issues causing a GM are primarily sourced to cementing errors in the early stages of the asset's lifecycle^{11,12,15,18}; accordingly, the AER indicates initial investments towards the longevity of an energy asset are central to well integrity.⁷ Although a sizable amount of research has aimed to characterize pathways that cause

SCVFs or GMs, identifying FG pathways is far more complex when a natural gas well is abandoned or undergoing abandonment.^{7,11-18, 21} Abandonment of a well introduces an additional pathway for fugitive releases, can exacerbate an existing infrastructure issue, can contaminate potable aquifers, and contribute to GHG emissions (Figure 1.1).^{15,16,18-20} Buried abandoned wells at a reclaimed site are cut and capped, so this thesis refers to the source of GM issues at this type of location as either the surface casing or production annulus. No true distinction can be made between SCVFs and GM releases, and thus any gas migrating through the soil is termed a GM. Additionally, in this thesis FGs exclude practiced/operational emissions; rather, the focus is on accurately detecting advective or diffusive gases, particularly free-phase CH₄, coming from the abandoned asset. The first of two studies in this thesis addresses fundamental practices for monitoring or detecting FGs at well sites, as described in the AER's recommendations for GM testing.

1.3. Alberta Energy Regulator recommendations for gas migration testing

GM and SCVF testing are the two main practices used in the industry to detect gases being unintentionally and uncontrollably released into the atmosphere.¹⁸⁻²⁰ Testing is also commonly performed when a well requires inspection or is approached for maintenance.^{19,20} GM testing is especially important for assessing abandoned assets where wellheads have been removed from the location and testing is restricted to surface measurements.¹⁹ Even if a wellhead is present, SCVF testing may be restricted due to safety concerns.^{19,20} Current regulatory guidelines require testing to be completed prior to commencing the abandonment of a well, and thereafter, but can be conducted at any point of a well's lifecycle.¹⁹ Testing procedures, equipment, and

techniques are all described in the appendix of the AER's *Directive 20: Well abandonment*. This document outlines the recommendations drafted by the Lloydminster Area Operations Group Gas Migration Team (LAOGMT) for both SCVF and GM testing.^{19,20} The LAOGMT is an industry-originated group influencing testing in the O&G industry since 1993.^{19,27} GM testing recommendations provided by the LAOGMT include a description of sampling point locations 30 cm from the wellbore, or buried abandoned wellbore, on opposite sides.¹⁹ Point locations are also placed at 2- or 1-m intervals from the wellbore every 90° up to 6 m, as well as any location within 75 m of the well where there is apparent vegetative stress (Figure 1.2).¹⁹

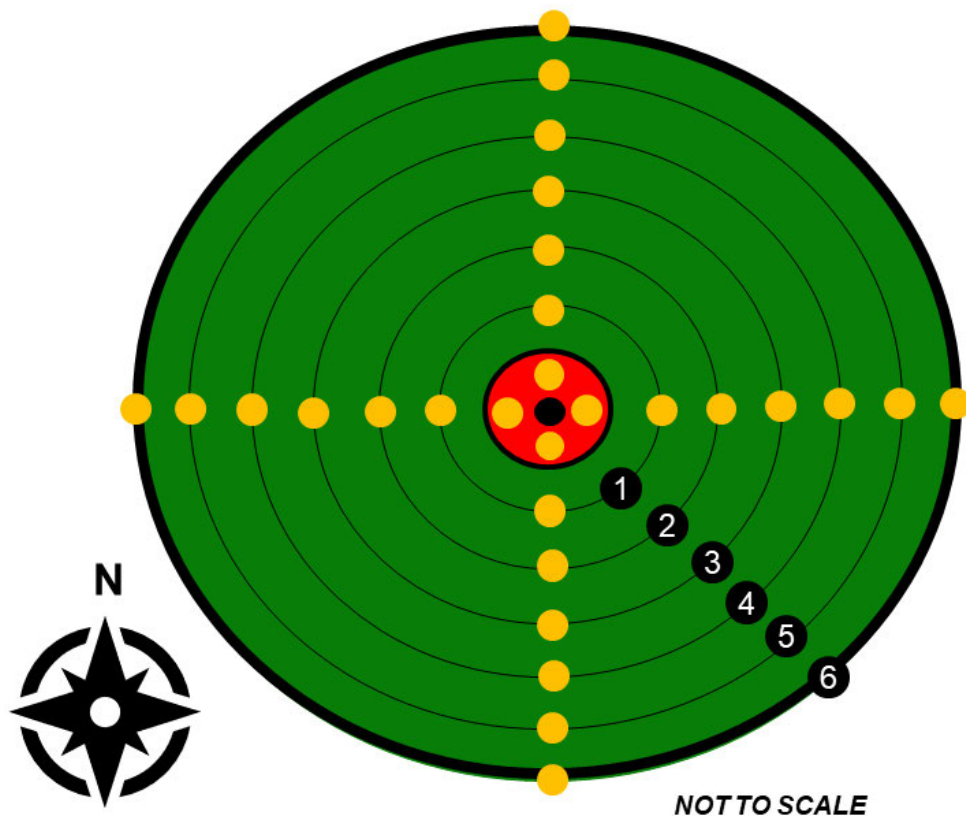


Figure 1.2. Schematic of sampling radius around an abandoned well centre at a field site. Red region indicates well centre sampling radius of 30 cm and numerically labelled black circles indicate distances in metres.¹⁹

This schematic approach is taken to ensure that gases are detected at intervals in each cardinal direction of the well centre as well as near areas of stunted plant growth, which is an established indicator of migrating gases.¹⁹ To promote optimal results, testing is not permitted during frost seasons as well as during and after rainfall.¹⁹ Sampling pattern is a minor topic addressed in this thesis. Discussion points analyze the effectiveness of this scheme and if variations such as increased directionality and sample size/distance demonstrate an increased probability of detecting FGs at point locations around the well centre.

AER recommendations indicate the type of tool placed at point locations around the well centre must be capable of reaching depths of 50 cm and have a diameter ≤ 64 mm; however, ground-disturbance regulations in Alberta restrict tools to 30 cm below the surface to ensure utilities are not exposed or damaged.^{19,28} Additionally, tools must have the means to seal surface holes or crevices while soil gases are drawn from the soil using an instrument.¹⁹ These tools can be broadly described as non-invasive surface techniques and invasive subsurface techniques. Literature to date only implicitly addresses which methodologies are ‘best practices’ in GM testing, with the majority of studies focused on projecting emissions from this sector. Surface techniques range from stationary domes to autonomous chambers.¹⁷ Subsurface techniques range from manually augured, sealed-off holes to metallic piezometers (vapour probes).^{16,19} Tools to be analyzed in this thesis for GM testing include domes for surface gas measurements and probes for subsurface soil gas measurements (Figures B.3). Study data will show that the choice of tool impacts what gases are reported in GM testing.

The AER also recommends required equipment for measuring gases on site. The document states the measurement of gases must utilize equipment that can detect combustible hydrocarbon concentrations as low as 1 percent of the lower explosive limit (%LEL) of CH₄ (5 %v/v).¹⁹ Detectors within the industry that report %LEL are commonly known as handheld portable multi-gas monitors.²⁸⁻³¹ The main marketed application of these portable monitors is to ensure air quality in the immediate surrounding environment meets the requirements for safe working conditions.^{29,30} FGs are a potential explosive hazard when an ignition source is nearby.^{29,30} Industry practices rely on these portable monitors to ensure the health and safety of workers in the environment; however, due to the vast acceptance of this tool throughout the sector, it is now the standard approach used for GM screening for government reporting.^{19,30,32} Hence, this thesis study integrates the use of these monitors, alongside the surface and subsurface sampling tools mentioned above, as a means to accurately detect FGs at the surface of an abandoned well site. Initial research presents limitations of these monitors for sampling in conditions with limited O₂.

Although not all recommendations for GM testing are reviewed in this thesis, the fundamental choice of sampling tool and detection carries considerable weight when reporting results to regulators and the AER, which updates databases open to the public for research.^{11,12,19} As mentioned, considerable knowledge gaps are related to sourcing stray gases at an abandoned well site. The first indication of a comprised abandoned well occurs during the decommissioning process. If a GM test fails to detect any issue, or releases are determined as nonserious, a fluid level test must be conducted to ensure integrity of the abandonment process.^{19,20} This final test ensures

that the seals properly block the natural gas reservoir from migrating to higher formations, contaminating groundwater, or the atmosphere.¹⁹ Once all doubts regarding abandoned infrastructure have been addressed, abandonment is completed and the land can be reclaimed.¹⁹ However, if a GM is identified as a serious risk to individuals or the environment, the well is then reentered into the abandonment process for remediation.^{19,20} Provincial regulators note that early decisions can mitigate failures and the costs incurred during remediation, which range from \$10,000 to \$1,000,000.⁷ A key component to remediating or circumventing stray gases is the use of scientifically based techniques and methodology to accurately detect and source damaged infrastructure during and after the decommissioning or abandonment of a well.^{7,11–15,18}

1.4. Detecting fugitive gases from natural gas wells

The main goals of GM testing are to accurately detect a GM at a natural gas well site and locate the formation or depth at which the source release occurs.^{7,19,20} Achieving these goals is not possible with current LEL detectors used in the industry; however, once elevated concentrations of combustible gases (>0 %LEL) are detected at a well location, remediating the issue is often outsourced to service companies.^{7,19} Companies within this industry utilize more sophisticated analytical techniques to detect FGs and trace them back to the source.^{7,18,20} Two types of indicators can be used with respect to a GM issue: concentration-dependent and concentration-independent techniques.

1.4.1. Concentration-dependent GM indicators

Common techniques that comprise concentration-dependent GM indicators are gas chromatography (GC) methods and, to a lesser extent, infrared (IR) methods.^{17,18} The AER, along with the United States Environmental Protection Agency, have long-established analytical techniques for researching and analyzing petroleum byproducts/contaminants.^{7,33} GC techniques are powerful and the best-known method for characterizing complex petroleum products.³³⁻³⁶ Profiling natural gas reservoirs emphasizes the analysis of CH₄ and heavier hydrocarbons such as ethane (C₂H₆), propane (C₃H₈), butane (C₄H₁₀), and pentane (C₅H₁₂).^{33,36-38} These gases are collectively summarized by the formula C₂₊. Natural reservoirs are characterized by high CH₄ with lesser but prevalent C₂₊.^{18,36} Conversely, CH₄ generated through biological processes is associated with trace, if not absent, concentrations of C₂₊ species and higher CO₂.^{18,36} Depending on whether natural gases originate from thermogenic, biogenic, or mixed sources impacts the compositional profile and indicates which gas species are useful to accurately characterize FGs at a well.^{18,36-37} In the area of interest particular to this thesis, natural gases have a mixed biogenic origin in source gases, also termed production zone, featuring high CO₂ and nitrogen (N₂) concentrations and trace C₂₊ species.³⁶⁻³⁷ Due to the varied compositional profile of natural gas reservoirs, GC techniques combine flame ionization detection (FID) to quantify hydrocarbon gases with thermal conductivity detection (TCD) to quantify other gases (CO₂, O₂, and N₂).^{34,35} Importantly, the lack of a proper procedure means gas from mixed bacterial origins can mislead interpretations of GM results. Sourcing the point of release of FGs in the subsurface requires more definitive concentration-independent techniques, such as stable isotopes.^{7, 36-37,39}

1.4.2. Concentration-independent GM indicators

The primary technique used as a concentration-independent GM indicator is stable isotopes. The Geological Survey of Canada has depended on isotopes to geochemically profile reservoirs and determine sources of contamination or conduct point-source monitoring.^{7,18,36,38} NRCan, along with the AER, also recognize as well as suggest technical GM testing methods such as stable carbon isotopes.⁷ Tracing isotopes in the soil subsurface is a method to match surface gases to production zone gases or overlying formations. Various stable isotopes can be applied in the petroleum industry, but the most common are ¹³C and deuterium (²H).^{7,36–39,41–43} A strength of this technique is the small gas sample volumes required to analyze the ratio of stable isotopes.⁴⁰ Interfacing GC with isotope ratio mass spectrometry results in an analytical method called compound specific isotope analysis.^{38,40} A carbon isotope value, or ‘signature’, is calculated with reference to an internationally accepted standard, Vienna Pee Dee Belemnite (VPDB). In this thesis, ¹³C is the most relevant and is calculated with the following formula^{37,43}:

$$\delta^{13}\text{C}_{\text{sample}} = \left(\frac{\left(\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{VPDB}} \right)}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{VPDB}}} \right) \times 1000. \quad [1]$$

Isotope values calculated are multiplied by a factor of a thousand and presented in units of per mille (‰) due to the lower abundance of ¹³C (1.1%) to ¹²C (98.9%) in nature.^{43,44} Equation 1 quantifies values by measuring the heavy isotope over the lighter.⁴³ A sample with a $\delta^{13}\text{C}\text{-CH}_4$ value of -50 ‰ contains less ¹³C (depleted) than a sample with a value of -40 ‰; conversely, a more positive value has more ¹³C

(enriched).⁴¹⁻⁴³ $\delta^2\text{H-CH}_4$ values are calculated in a similar manner with the heavier isotope (0.01%) over the lighter (99.9%) using the Vienna Mean Standard Ocean Water (VMSOW).^{41,42,44} The main advantage of applying stable isotopes in GM testing is the unique source signatures of CH_4 that naturally occur in the environment (Figure 1.3).⁴¹⁻⁴⁴

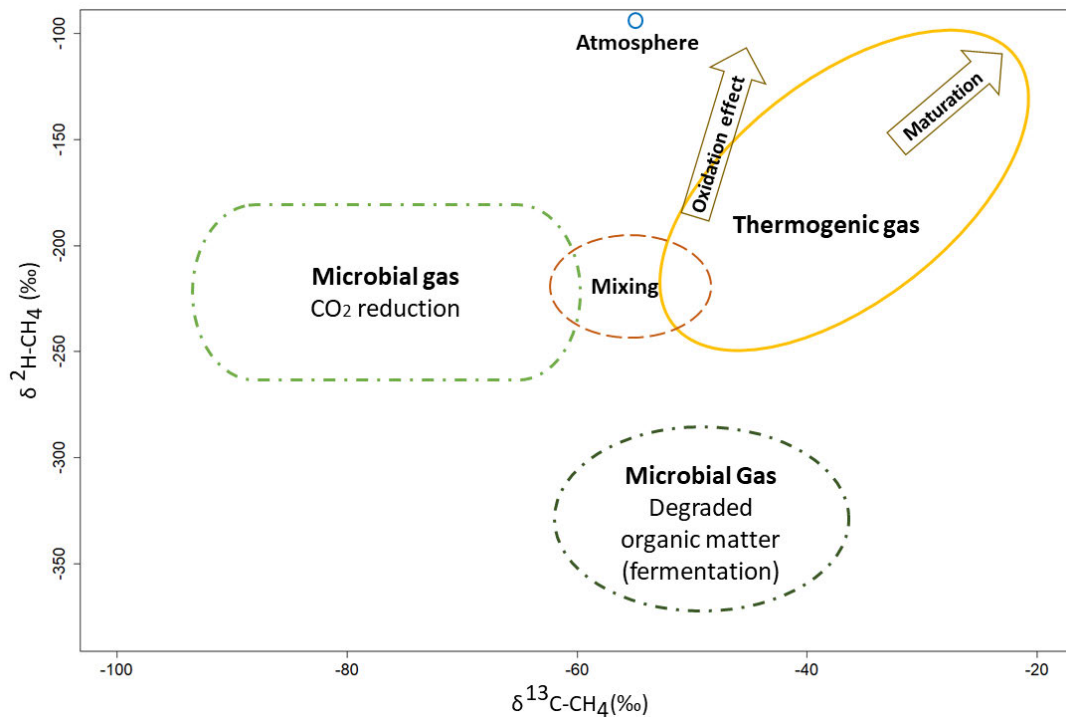


Figure 1.3. Carbon and deuterium stable isotopic signatures of natural CH_4 sources in the environment.^{40,41}

1.4.3. Fractionation and isotopic effects

Separation of CH_4 sources is based on the mass-dependent isotope fractionation effects, which is influenced by both biological and thermal processes in the soil.⁴⁵ Fractionation alters the isotopic composition in a given sample, particularly soil gases.^{41-43,46-47} The main type of fractionation effect on which this thesis focuses is the observed kinetic isotope effect (KIE) when CH_4 is oxidized to CO_2 (Equation 2)^{18,41-42,46}:



Due to the difference mass of ^{13}C and ^{12}C the zero-point energy of the heavier isotope causes a larger energy barrier for bond breaking, microorganisms (methanotrophs) in the soil preferentially oxidize or consume the lighter carbon isotope of CH_4 over the heavier.⁴⁶⁻⁴⁷ This also occurs in naturally sourced CH_4 produced by methanogens, which is compositionally more enriched in ^{12}C .⁴⁶⁻⁴⁷ Natural gas reports highlight $\delta^{13}\text{C}-\text{CH}_4$ values alongside $\delta^2\text{H}-\text{CH}_4$, as both tracers have considerable overlap with natural or biologically altered sources.^{38,41-43} Companies in Alberta specifically keep a record of $\delta^{13}\text{C}$ isotopes of formations in specific regions to provide concise analytics for operators and industry leaders when called upon to identify GM coming from a specific formation and subsequent depth.⁷

For the same reason that concentration-dependent techniques cannot always accurately identify the source of an uncontrolled release, concentration-independent indicators cannot always quantify the severity of a GM issue if one is detected. Both indicators provide a means of addressing the limitations of the other but are subsequently impacted by the same contamination sources. The choice of sample media for GM testing is heavily dependent on invasive, subsurface measurements. Soil gases are innately complex as they represent a part of the puzzle in a GM issue due to alteration of gases migrating through the soil subsurface.^{17,18} Unintended release of gases in the soil can be altered both compositionally (Figure 1.2 and Equation 2) and chemically (Figure 1.3 and Equation 1) within a single sample of gas.^{23-25,45,46} Contamination can propagate greater uncertainty in both measurements and can cause misidentification of a GM issue.^{17,18,33} These impacts are dependent on

environmental factors that are specific to a given well location and cannot be generalized for all natural gas well sites. Depending on the risk assessment procedure, these indicators can accurately identify a GM issue at an abandoned well site or misguide interpretations due to interferences innate within this type of sample medium. The main concern and focus of the second study in this thesis are current AER risk assessment procedures that indicate any point location measuring above 0 %LEL is indicative of AGM.⁷

1.5. Risk assessment practices in GM testing

The approaches thus far aim to circumvent misinterpretations are countered by normalizing the various complexities in GM results. Risk assessment guidelines indicate the confirmation of whether a GM issue is present at a given well site often depends on a single sample or sample-to-sample interpretation from GM test results. Site assessments adopting this framework originate from regulatory requirements qualifying any sampled location above explosive concentrations (0 to 5 % v/v) of CH₄ as indicative of GM.^{7,19,20} Topics in the literature on the natural gas sector focus on predicting GHG contributions to determine global warming impact.^{11-14,17} Thus far, current risk assessment methods use geochemical techniques in the subsurface with graphical representations or linear modelling techniques.^{7,18,36-39} Profiling composition or stable isotope data uses cross plots to categorize or source field samples.^{18,36-39} A common example of this compares CH₄ plotted against ethane or C₂₊, which often exclusively includes ethane and propane.¹⁸ These plots facilitate the identification of gas samples characteristic of thermogenic gases, containing higher concentrations of C₂₊ than biogenic gases, and can be a sensitive indicator of the gas

source.^{18,36} For the same reasons as concentration-dependent indicators, stable isotopes are used as a more effective means to discern the source once samples have been filtered. The assessment of stable isotope data in GM testing often utilizes Schoell or Whiticar style plots (Figure 1.3).⁴¹⁻⁴² These plots differentiate sources by first marking regions that indicate the isotope ranges of $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ of sources on a graph before plotting data points.^{18,33,36-39,41-42} Source identification can then be easily visualized once the data are plotted. Variations of Schoell plots combine gas composition with the stable isotopes to analyze possible concentration trends.^{36,38} Approaches to risk assessment through graphical representations are quite limited since it cannot account for the various interactions or constituents within soil gas samples. Multi-variate techniques are required to interpret multiple variables, but no literature presents the use of such techniques to interpret contamination interactions in GM testing. The few techniques that have been introduced are based on math and statistics.^{17,18} Identification of background and thermogenic gases in a GM testing has been achieved through averaging site gases at control sites and using standard deviations from the mean as a threshold to differentiate between the two sources.¹⁸ Another independent study utilized averaged gas concentrations from various sites and applied analysis of variance (ANOVA) to determine if concentrations were statistically different from control site compositions.¹⁷ In this thesis, the second study introduces a chemometrics tool used in environmental contaminant tracking to normalize interferences within soil gases and uncover concealed information in GM data collected at an abandoned well site.^{33,48-49}

Principle component analysis (PCA) is a common multivariate method utilized in various disciplines and has been renewed multiple times with each novel application in diverse scientific fields.^{33,48-49} PCA is primarily used as an exploratory tool to reduce the complexity of multivariate data to a simplified framework with the ability to maintain data integrity; it is often an intermediate step in modelling.^{33,49} For example, PCA is often applied in petroleum engineering for the purpose of projecting production estimates using multiple factors within petroleum goods.⁵¹⁻⁵² In these cases PCA combined with post-process modelling approaches has been used to forecast production using rate-time data to generate predictor models.⁵⁰ More specific to this thesis, a study from the Saskatchewan Geological Survey applied PCA to distinguish certain hydrocarbon components impacted by biochemical, sedimentological, and physical processes to characterize petroleum-source rock 'families'.⁵¹ Most importantly, PCA has shown to be an effective tool for the environmental fingerprinting of sources of oil spills using 26 variables that represent components ranging from C₅ to C₃₀.⁵¹ PCA presents great strength as an exploratory, investigative, and source interpretation tool for petroleum tracers to classify and determine reliable constituents and logically lead further exploration of this natural resource.⁴⁸⁻⁵² This thesis work demonstrates a novel application of geochemical tracer techniques in multivariate modelling as a risk assessment tool to accurately detect GM at an abandoned well site. PCA modelling used in GM testing can assist interpretations, which are heavily impacted by multiple contamination sources, in the hopes of reducing false-positive and/or false-negative results in AER reporting. This

will subsequently increase monitoring accuracy, reduce testing inaccuracies and remediation costs, and improve emissions estimates for abandoned well sites.

1.5.1. Principal component analysis

The first step of PCA is to transform the data by standardizing the input matrix ($n \times m$) for the GM dataset. Soil gas components (m) are standardized by calculating the mean of each given gas constituent, subtracting sample locations (n) containing the gas, and dividing by the standard deviation.^{33,48} Transformation using this method is primarily meant for statistical purposes to ensure equal variance, such that the mean of each variable (gas constituent) is 0 and the standard deviation is 1.³³ The second step of PCA reduces datasets through singular variable decomposition (SVD) to assess the dynamics of multivariate data to determine what is redundant or noise and project the data into uncorrelated reference frames called principal components (PCs).^{33,48} Selection of PCs for visualization is determined through SVD, which takes the normalized multivariate dataset—matrix \mathbf{X} ($n \times m$) with rows (n) representing soil gas samples at various locations in a field site and columns (m) corresponding to a single gas component concentration measured in the soil gas sample—and generates PCs with the following matrix decomposition^{33,48}:

$$\mathbf{X} = \mathbf{U} \mathbf{\epsilon} \mathbf{V}^T, \quad [3]$$

where the orthogonal matrix, \mathbf{U} , diagonal matrix, $\mathbf{\epsilon}$, and orthogonal matrix, \mathbf{V}^T , represent decomposition of the matrix \mathbf{X} by a rotation, stretch, and another rotation, respectively. The diagonal matrix contains the PC eigenvalues, in decreasing order.^{33,48} Information gained from SVD calculates new values for the original data points, called scores.⁴⁶ PC loadings determine the contribution or influence of each

variable (soil gas components) and eigenvalues simplify selection of the PC axis by retaining the most meaningful axes.^{33,48} By selecting the axes that retain greater variance, or meaningful eigenvalues, more information from the original dataset is retained.^{33,49} This comprises the third and final step of PCA, in which the resultant graphical representation or biplot is an ‘accurate’ subset of the original dataset⁴⁸; this gives the user a simplified, often 2-dimensional (2D) means of interpreting a multivariate dataset without compromising data integrity.⁴⁹ To further bring out the hidden properties of the data, this thesis utilizes hierarchical clustering tools to determine the number of cluster centres, using partitioning around medoids (PAM), in a given PCA biplot and then grouping the data with the selected number of cluster centres with K-means clustering.^{49,52} Interfacing these two mathematical and statistical tools will produce groupings of soil gas samples taken around the well centre that are highly correlated and statistically significant.^{33,52} Grouping highly correlated samples can collectively reveal true site geochemical characteristics that would otherwise be difficult to obtain with single-sample or sample-to-sample interpretations. Using this multivariate tool levies the decision-making process in risk assessment towards data results and away from interpretations based on commercial laboratories.

1.6. Hypothesis and objectives

Current GM testing practices recommended by the AER will be addressed in the second chapter by testing the following hypotheses:

- 1. Surface-based measurement techniques are not as effective as subsurface-based measurement techniques for identifying elevated concentrations of CH₄ around an abandoned well.*
- 2. Industry standard equipment, such as a handheld portable multi-gas monitor, is not as appropriate for measuring elevated concentrations of CH₄ in GM testing as it is for alerting workers to atmospheric hazards in a workspace.*

Risk assessment practices in GM testing will be addressed in the third chapter by testing the following hypotheses:

- 1. Risk assessments from previous GM tests using single-sample or sample-to-sample interpretation of concentration and isotope data do not provide assessments that are as accurate and definitive as those using a multivariate approach to interpret concentration and isotope data.*
- 2. GM testing recommendations set out by the Alberta Energy Regulator that rely on reporting of at least 1–2 samples to substantiate a GM issue are not as effective or reliable as tests with sample sizes >5 for gas composition and gas stable isotopes.*

Hypothesis testing will be conducted by evaluating results from two GM tests completed in 2014 and 2019 at the same abandoned well site in Western Canada. The results of this work will be formulated into ‘best practices’ and framed to be

seamlessly added to current AER recommendations for GM testing. These revised practices will in turn provide accurate industry monitoring, reporting, and quantification of GHGs from the natural gas sector.

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CHAPTER 2

GAS MIGRATION TESTING AT AN ABANDONED WELL SITE IN WESTERN CANADA

2.1 Introduction

Reducing methane (CH₄) in the atmosphere is key to stabilizing global temperature rise.^{1,2} With a global warming potential (GWP) of 86 over a 20-year timeframe, CH₄ has a greater ability to warm the Earth's atmosphere than CO₂ on the same timescale.¹ For this reason, CH₄ is an important focus in efforts to meet Canada's current climate change goal.² The majority of Canada's emission contributions to the atmosphere originate from the oil and gas (O&G) sector.^{2,3} Natural gas from this sector constitutes 44% of the CH₄ released into the atmosphere, with the remainder sourced to agriculture and solid waste disposal.^{2,3} The majority of Canada's natural gas wells are in Alberta, where releases have been estimated to account for 70% of CH₄ emissions.^{2,3,4} These releases primarily originate from venting and flaring practices, with the remainder due to unintended releases.^{2,3} Practiced emissions have since (as of 2017) undergone regulatory changes, but fugitive gases (FGs) remain a concern²; in particular, 6–14% of emissions are sourced to abandoned wells.^{5–8} Research in this sector has identified two pathways for unintended releases from natural gas wells.^{5,7,9,10} The first is surface casing vent flow (SCVF)^{9–11}, which results from well integrity issues that cause the collection of gases in the surface casing of the wellhead.¹⁰ These collected gases are either vented or directly released from the wellhead to the atmosphere.^{5,10} The second is gas migration (GM) due to various types of defects in a well, but is primarily distinguished from

SCVF due to gases escaping into the adjacent soil environment.^{5,9,11} Discrimination between these two release pathways and infrastructure becomes an even greater challenge when a well is abandoned.^{9,11} Emission estimates from energy assets have been highlighted as an area in need of improvement in open databases provided by the Alberta Energy Regulator (AER), especially when tracing unintended releases.^{5-7,9} The focus of this study is to improve CH₄ emission estimates in the natural gas sector, specifically from abandoned wells.

Emission reporting of FGs from a well is primarily achieved through standard industry tests. Testing at a natural gas well can be completed at any stage of a well's lifecycle, but is most important right before and after an energy asset is decommissioned.¹² Before the abandonment process begins, a well must be tested to ensure zero gas flow to the surface, as otherwise it could represent a worker, public, or environmental hazard.^{12,13} AER *Directive 20* provides recommendations for testing well sites for FG during well abandonment.¹² This document outlines regulatory guidelines for well abandonment with procedures, equipment, and methodology for testing well integrity and contains recommendations on two different techniques for detecting FGs: SCVF and GM testing.¹²

Well infrastructure failure can be determined by measuring the SCVF.¹² A bubble test is completed on the well assembly by monitoring the flow in the surface casing, an engineered barrier that protects potable aquifers.^{5,10,12} The AER mandates that any bubble test indicating a flow rate greater than 300 m³/d requires repair.¹³ SCVF testing is an accessible and easily quantifiable means of determining well failure; however, assemblies for testing are not accessible when the energy asset is

abandoned.^{11,14,15} Therefore, when a well has completed the abandonment process and either an infrastructure or abandonment failure occurs, testing is limited to the surface of the abandoned well site.^{12,13} GM testing primarily assesses FGs at the surface of a well site that have escaped the exterior barriers of the well.^{9,11,12} Once released from the confines of the wellbore, gases migrate through the soil via various pathways in the subsurface or soil environment.⁹ Testing a well site for FGs is conducted radially, in all cardinal directions, up to 6 m from the well centre (if abandoned) or wellhead at a soil depth of 50 cm.¹² In practice, depth measurements are limited to 30 cm due to ground disturbance regulations that protect buried utilities.¹⁶ Regulatory requirements for reporting FGs at a well site indicate percent lower explosive limit (%LEL) measurements of combustible hydrocarbons.^{12,13} By AER standards, measurements above 0 %LEL are evidence of active GM at the test location.^{5,13} Reporting values in this manner assists in determining if a GM issue is serious or non-serious.¹³ A serious GM features %LEL measurements that indicate an explosive, asphyxiant, or environmental hazard.¹³ Studies reporting on GM testing reveal the complexities in confirming an active GM issue, arising from either an SCVF or GM pathway, and in these instances are more reliant on samples collected from SCVF to confirm an active GM (AGM).^{9,11,14,15}

The first GM testing recommendation of this study evaluates the sampling approaches used to measure FGs at a well site. The literature presents a variety of tools for assessing FGs, broadly categorized as non-invasive, for measuring surface gases, and invasive, subsurface tools for measuring soil gases. Non-invasive tools rest at the soil surface of a well site and can range from passive, stationary domes to more

sophisticated, automated chambers for sampling FGs.¹⁴ Invasive tools are submerged in the soil at a predetermined depth and can vary from augured holes around the well centre or simple stainless steel probes to digital data loggers buried in the soil.^{11,14} This study assesses two basic, cost-effective sampling tools for monitoring FGs at an abandoned well site: domes for surface gas measurements and probes for measuring soil gases (Figures B.3). Comparison of results obtained from these two tools reveals an important difference in gases quantified around abandoned well sites.

The second AER recommendation this study investigates evaluates the detection equipment used to quantify FGs in %LEL around the well centre.¹² The most common detector used in the industry is the handheld portable multi-gas monitor, the primary marketed purpose is to ensure worker safety and alert individuals if the surrounding atmosphere is becoming hazardous to their health.¹⁷⁻¹⁹ Alerts are programmed into the monitor to indicate if the immediate atmosphere is potentially toxic for breathing or combustible when an ignition source is present.^{18,20} However, due to their wide acceptance in everyday practices, these monitors have become standard equipment for reporting stray gases from natural gas wells.^{5,11,12} These monitors are typically manufactured with a catalytic combustion (CC) detector or sensor that analyzes total hydrocarbons.¹⁷⁻²⁰ Manufacturers typically standardize CC detectors to the LEL of CH₄, at 5 %v/v, which corresponds to 100 %LEL.¹⁸⁻²⁰ Hence, concentrations greater than 0 %LEL (0 %v/v CH₄) and up to 100 %LEL (5 %v/v CH₄) indicate the presence of GM at a well site.^{5,12} Applications related to GM testing include surface analysis of gases at a well site, known as ‘sniffing’, and are beyond the manufacturer’s intended use. Technical studies on this type of detector reveal the

shortcomings of CC sensors. Specifically, detection of gases is done by igniting hydrocarbons in the presence of oxygen (O₂) using a metal catalyst.^{19,20} Measurement variability arises when samples with O₂ content less than 10 %v/v may not provide sufficient reaction conditions for combustion of gases.¹⁸⁻²⁰ Additionally, this detector type has a limited detection range of 0–5 %v/v and sensor response is saturated at the LEL of CH₄ (100 %LEL = 5 %v/v).^{18,19} The accuracy of the detector response to concentration declines thereafter and the sensor is shut off as a safety mechanism to maintain operating lifetime.^{19,20} Even though manufacturers calibrate the sensor to CH₄, quantities reported are non-specific in response to the hydrocarbons being sampled.^{18,20} The attractiveness of this monitor for GM testing is understandable as the user is alerted to FG readings >0 %LEL and an alarm sounds at 100 %LEL, indicating a serious GM issue at the surface of a well site.^{13,18,19} Hence, this detector encounters unique limitations in terms of GM testing, which preferentially implements subsurface sampling tools; thus, restrictions and ‘best practices’ need to be in place with respect to testing procedures using a portable monitor. This study presents data for framing the limitations and additional precautions required when using portable monitors for GM testing to ensure accurate reporting and assessment at abandoned well sites. The portable monitor was evaluated using both sampling tools (domes and probes), with results compared to more sophisticated detectors to articulate the limitations of CC detectors in GM testing. Results from this comparison are used to propose best practices for detecting and sampling FGs at a well site, the aim of which is to reduce CH₄ emissions through better detection and monitoring of unintended emissions at abandoned well sites.⁵

Assessments of AER recommendations reported in this study are the result of two GM tests completed post-abandonment in 2014 and 2019. Sampling tools were placed side-by-side at various locations around the well centre of the site (Figure B.3). At each location, quantification of CH₄ was completed using an industry standard portable monitor with results compared to another type of field detector. Both investigations also collected soil gases on-site and analyzed them in a laboratory on a gas chromatograph (GC) to confirm field measurements. Test results prompted further experimentation to assess the feasibility of portable monitors for conducting subsurface measurements, where lower O₂ concentrations are common. These analyses provide evidence of the limitations of portable monitors outfitted with CC-type sensors and offer additional practices to be integrated into the AER's recommendations. Our findings aim to improve GM testing recommendations and equip regulators with more accurate tools and approaches for assessing FGs at abandoned wells sites.

2.2 Materials and methods

2.2.1 Field materials and methodology

2.2.1.1 Soil gas collection and storage

Soil gas locations [REDACTED]

[REDACTED]

[REDACTED] Gas was sampled with a 60-mL gas-tight syringe and then transferred to a sterile, evacuated 60-mL serum vial.

[REDACTED]

[REDACTED]

[REDACTED] Each location was left to stabilize for >1 h. Dome locations were analyzed prior to soil probes using an Agilent 490 Micro GC system. Soil gas was initially sampled using a 60-mL gas-tight syringe. After syringe sampling, site locations were analyzed using a portable four-gas monitor in the same order. Samples were collected with 60-mL syringes fitted with a three-way Luer-lock valve to prevent contamination between samplings. Soil gas samples were screened prior to storage in 60-mL sterile and evacuated serum vials (Wheaton Glass).

2.2.1.2 Soil gas analysis

Soil probe gas samples from the 2014 field program were analyzed at the University of Calgary. Uncertainty in reported soil gas concentrations is 5% of chromatograph peak area. Soil gas measurements reported for 2014 were completed using a portable analyzer with an infrared (IR) sensor. The analyzer detection range for both CH₄ and CO₂ was 0–100 %v/v; uncertainty for measurements between 0 and

5 %v/v was ± 0.3 %v/v for both gases and for measurements between 0 and 70% for CH₄ and 0 and 60 %v/v for CO₂ was ± 0.5 %v/v.²¹

Soil gas measurements in 2014 and 2019 were completed using a handheld portable multi-gas monitor, marketed as the RKI Eagle 2 (Figure D.4), with a detection range for CH₄ of 0–5 %v/v (0–100%LEL), O₂ of 0–40 %v/v, CO₂ of 0–60%v/v, and H₂S of 0–100 ppm.¹⁷ Measurement uncertainty for these gases was $\pm 5\%$ of reading for CH₄, CO₂, and H₂S and $\pm 0.5\%$ of reading for O₂.¹⁷

Soil gas samples from the 2019 field program were screened using an Agilent 490 Micro GC system (Field GC). Gas samples were injected at 110 °C. O₂, N₂, and CH₄ were separated on a MolSieve 5A (MS5A) 10-m column at 80 °C and a constant pressure of 29 psi. CO₂ was separated on a PorPLOT U (PPU) 10-m column at 50 °C at a constant pressure of 45 psi. The column carrier gas was helium (He) purchased from Praxair Canada Inc., and the system featured thermal conductivity detectors (TCDs). Quantification of soil gases on-site was completed using a programmed external calibration curve generated, prior to field implementation, using laboratory standards. Curves were generated for CH₄, CO₂, N₂, and O₂. Screening and storage of samples was conducted for soil gases that contained CH₄ and CO₂ concentrations greater than 0.1 %v/v. Analytical error in reported concentrations was not quantified for this method.

Soil gas samples stored in serum bottles in 2019 were analyzed commercially at the University of Windsor. Gas composition was analyzed on an Agilent 7890B GC (lab-based GC) equipped with three channels for gas analysis: Channel 1 outfitted

with a flame ionization detector (FID) to quantify hydrocarbons and methane (CH₄) and Channels 2 and 3 outfitted with TCDs for CO₂, N₂, and O₂. Analytical error was 5% of the integrated peak area of the gas species and the method detection limit was 10 ppm (0.001 %v/v).

2.2.1.3 Sources of error

The main source of error in reported concentrations of CH₄ is dilution from atmospheric interactions due to connections between the probe and syringe, contamination by degraded organic matter, or microorganisms in the soil. To avoid excessive dilution of gases during sampling, soil push probes were buried in the subsurface with a manual downward force and packed tightly around the point of entry. Sampling of soil gases was completed using gas-tight syringes, purged for both dome (140 mL) and probe (5 mL) sampling prior to analysis on the Agilent 490 Micro GC.

To reduce prolonged, unrepresentative sampling (oversampling) of gases in soil, point locations were initially sampled and analyzed on the Agilent 490 Micro GC prior to sampling using a portable multi-gas monitor. Sampling with a syringe required less volume than the portable monitor, which draws sample at 944 mL/min.¹⁸ This reduced the potential evacuation of soil gases from any point location and ensured the best accuracy in characterizing soil compositions with analytical techniques.

To present the most accurate estimates for field measurements, soil gas concentration values are reported as non-normalized. Concentrations reported from laboratory analyses are presented as normalized concentrations after quantification

using an external standard method, calculated based on species detected in the sample. Field GC results are presented as concentrations directly calculated from external standard calibration curves. Normalized soil gas compositions of field GC measurements have a higher percent error (22.0%), lower accuracy, than the same measurements non-normalized (18.0%) to gas species in the sample when compared to lab-based GC concentrations analyzed at identical point locations (Table C.5).

2.2.2 Laboratory materials and methodology

2.2.2.1 Calibration test standards

Calibration testing of the portable monitor was completed using ultra high purity (UHP) certified CH₄ standards (Praxair Canada Inc.) at concentrations of 1.04 and 2.96% v/v with N₂ balance and containing no O₂. Calibration using a standard with oxygen was completed using a certified standard cylinder containing 2.5 %v/v CH₄, 12 %v/v O₂, and 25 ppm H₂S with a N₂ balance (Premier Safety).

2.2.2.2 Calibration test method

Calibration testing of the portable monitor was completed using manufacturer recommended methods, both passive and active. Passive gas delivery utilized Tedlar® gas bags (500, 1000, and 3000 mL; Concept Controls). Active gas delivery utilized a demand flow (DF) regulator (6 L/min; Premier Safety).

For passive calibration of the portable monitor, a standard gas was transferred to the gas bag and connected to the portable monitor probe in calibration mode after the set value of the standard gas was entered. DF calibration was completed by connecting a hose from the regulator to the portable monitor probe until a stable measurement was achieved; this value was used for the calibration check, after which

the span adjust was reported. The minimum adjusted value recorded in these calibrations was 6,000 ppm (0.60 %v/v); the maximum recorded was consistently 50,000 ppm (5.00 %v/v), except for the lowest standard that reported 15,500 ppm (1.55 %v/v). Span adjustment represents the value to which the sensor response could be corrected during the calibration of the sensor.

After calibration, measurements of standards were conducted in continuous monitoring mode and performed in triplicate using a 1-L gas bag. Concentrations of CH₄, O₂, H₂S, and CO₂ displayed on the portable monitor were recorded every 30 s until the gas bag was depleted. Measurements from three trials are presented as average ± standard deviation. Each experiment began immediately after the bag valve was opened, with the portable monitor probe hose connected to the opening. Time to deplete the gas bag of its contents was consistently 2 min 30 s.

A data quality check was performed with the 3-L gas bags using the DF regulator calibration test conditions. Three bags were designated for each standard. Measurements of standards in continuous monitoring mode were performed as described above. Prior to the connecting the gas bag to the probe, a subsample of the gas bag was taken for GC analysis. The bag was then connected to the hose attached to the portable monitor, the bag valve opened, and the concentrations of four gas components recorded. This test was also completed in triplicate and measurements averaged. Time for bags to be depleted ranged from 5 to 6 min after the bag valve was opened. Gas bags used in the calibration were tested in a similar manner; however, only one trial was collected for each to ensure the integrity of measurements reported in test results.

All gas bags used in testing were purged three times, at half volume, with standard gas before performing any portable monitor calibration or continuous measurements. All values presented in this work were generated in continuous monitoring mode of the portable monitor with CH₄ and H₂S reported in ppm and O₂ and CO₂ in %v/v.

2.3 Results and Discussion

2.3.1 Domes vs. probe GM sampling tools

Initial evaluation of AER recommendations was based on implementing sampling tools in a side-by-side comparison at selected point locations around the well centre (Figure B.3). In both the 2014 and 2019 GM tests, domes and probes were placed at a location, left to equilibrate, and then gases sampled using a portable monitor. Measurements of CH₄ concentration in domes (surface gas) and probes (soil gases) were then compared to determine which sampling tool represented the best practice for GM testing.

Surface gas measurements in 2014 detected CH₄ concentrations ranging from [REDACTED] at various locations around the abandoned well (Table 2.1). The highest soil gas CH₄ concentration [REDACTED] was detected [REDACTED] of the well centre and the lowest ([REDACTED]) [REDACTED]. A single location [REDACTED] of the well centre was below the detection limit (BDL) of the portable monitor; otherwise, CH₄ was detected [REDACTED] from the well centre. Soil probe gas concentrations, measured at a depth of 50 cm, were 50- to 62-times greater than values reported at the surface (Table 2.1). Soil gas measurements were [REDACTED] [REDACTED] of the portable monitor 1 to 5 m from

the well centre; concentrations at these locations cannot be quantified accurately by the portable monitor. [REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

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[REDACTED] GM testing using domes increases the potential for environmental interferences to impact surface gas measurements. Underestimated CH₄ concentrations could result from atmospheric contamination diluting gases at the surface or the suppression of gases in the subsurface due to soil hardening or freezing following seasonal changes.¹ [REDACTED]

[REDACTED] elevated CH₄ in the subsurface could also be due to degraded organic matter in the soil.^{22,23} The number of locations with elevated CH₄ concentrations indicates further testing is required to determine the source.

In 2019, a notable difference in surface and soil gas CH₄ was observed (Table 2.2). Side-by-side comparison of the approaches was completed similar to 2014; however, point locations were sampled at a depth of 30 cm and were restricted to 3 m from the well centre (Figure B.3) due to the presence of standing water. In this GM test CO₂ concentrations were also measured. Dome measurements of surface gases indicated CH₄ concentrations BDL of the portable monitor (0 %v/v). [REDACTED]

[REDACTED] (Table 2.2). [REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED] Soil suppression and atmospheric contamination are potential factors interfering with surface detection and appear to be reduced when probes are submerged in the soil immediately beside the surface domes. Another factor potentially reducing CH₄ detected at the surface in 2019 was the water that surrounded the well centre.⁹

This simple side-by-side comparison of sampling tools in two separate GM tests indicates an important difference that impacts the quantification of FGs at abandoned well locations. Our results consistently show that subsurface tools, such as probes, are the best practice in GM testing. Invasive techniques reduce the impact of environmental interferences for quantifying CH₄ and provide greater evidence of an AGM. [REDACTED]

[REDACTED] Due to the large difference between dome and probe measurements, it is reasonable to consider a source of error in the portable monitor measurements is attributed to the detector type (CC). Hence, additional detectors were implemented during GM testing to assess the accuracy of CH₄ concentrations reported by the portable monitor.

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2.3.2 *Soil gas detection equipment*

Measurements for probe soil gases from the portable IR analyzer and TCD detector (Field GC), collectively referred to as field equipment, were generally more comparable to laboratory GC (lab-based GC) values than those measured with monitors featuring CC detectors (Tables 2.3–4). Field GC concentrations were the most accurate, with 18% difference between lab-based results in 2019, and portable analyzer CH₄ measurements presenting 20% error in 2014. Some variability may have been due to analysis timing, i.e., if field equipment measured locations prior to or after sampling for lab-based GC analysis. [REDACTED]

[REDACTED] Measurements reported by field equipment after sampling for lab-based GC analysis may reflect locations with soil gas CH₄ already evacuated.

[REDACTED]

Observed differences in results, with respect to detector type for soil gas measurements, begin to distinguish best practice techniques. Detection of CH₄ and CO₂ with a portable IR analyzer uses dual wavelength IR for measurements and field GC detection with TCD provide more accurate results in field applications; however, the cost of this instrumentation is often prohibitive for routine gas migration

investigations.²⁶⁻²⁷ The most commonly used and economical CH₄ detection approach are CC-based portable monitors; [REDACTED]

[REDACTED]

[REDACTED]

The use of portable monitors with CC detector as a worker safety tool is well established; however, determining the severity of a GM issue at an abandoned well site is not a well-defined application. The guidelines for CCDs suggest measurements are not accurate when oxygen concentrations are below 10 %v/v.¹⁸ Higher quality gas migration samples target low levels of atmospheric contamination. Subsurface soil gas concentrations that are not contaminated by atmosphere should have low concentrations of O₂ and can often have high concentrations of N₂. AER *Directive 20* guidelines do not specify detector type or requirements to disclose detector type and specific concentrations of gases beyond reporting LEL measurements. Hence, this thesis will investigate the performance of CC detectors under unfavorable gas concentration conditions.

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2.3.3 Calibration of portable monitor for soil gas detection

Laboratory calibration of the CC detector was completed via two gas delivery methods as recommended by the manufacturer. These methods deliver gas either actively, with a flow rate, or passively, with no set flow rate, to the monitor. The CC sensor was first calibrated using the passive delivery method, with a gas bag. Manufacturers recommend O₂ concentrations between 10 and 16 %v/v for calibrating the CC detector.¹⁸ In this experiment the sensor was calibrated using a 25,000 ppm CH₄ standard with 12 %v/v O₂. Once passive calibration was completed, this step was switched to the active method with a DF regulator. After each calibration, the

monitor was used to measure three pre-selected standards in continuous monitoring mode, completed in triplicate, and averaged for each experiment (Table 2.5).

Soil gas standards used in continuous monitoring were selected to replicate conditions routinely found at GM sites, but outside the range of a CC detector. Standards selected for replicating non-ideal conditions contained CH₄ balanced with N₂, representing the extreme case of soil gases containing no O₂. Ideal conditions represent surface monitoring surrounding the well centre, where sufficient O₂ is present from atmospheric gases. Certified CH₄ standards (low-, middle-, and high-range) were selected to calibrate the portable monitor. These denote the ppm (% v/v) values relative to one another such that the low-range standard has a certified CH₄ concentration of 10,400 ppm (1.04 %v/v), mid-range standard of 25,000 ppm (2.5 %v/v), and high-range standard of 29,600 ppm (2.96 %v/v). The standard selected to replicate ideal conditions was the mid-range standard, which contained 12,000 ppm (12 %v/v) O₂, while non-ideal conditions were replicated using the low- and high-range standards, both balanced with N₂.

The mid-range calibration returned the best results for reporting CH₄ measurements (Table 2.5). Measurement of the low-, mid-, and high-range standards resulted in values with respective percent errors of 55 (underestimate), 30 (overestimate), and 86% (underestimate) with respect to the certified concentrations. Surprisingly, the CC detector did not always reproduce values of the mid-range calibration gas when the same gas was used as a test gas. Measurements of the standard with O₂ resulted in overestimates (Table 2.5); however, presence of O₂ appears to be an important component for CH₄ measurement accuracy.

To determine if the underestimated CH₄ measurements were due to the use of a passive delivery method for calibrating the monitor, a DF regulator was subsequently used to calibrate the monitor. The same data collection procedure was followed for mid-range calibration and measurements for all three standards were completed in triplicate using gas bags for sampling (Table 2.6). Test results indicate improved sensor response (26,607 ppm) to the CH₄ standard (25,000 ppm) used in the calibration step (overestimate, 6% error). However, the low- (3,753 ppm) and high-range (3,423 ppm) CH₄ standards remained grossly underestimated with measurement errors of 64 and 88%, respectively, which were similar to the results from gas bag calibration testing (Table 2.5).

These experiments suggest the portable monitor is capable of detecting CH₄ but, in the absence of O₂, reports erroneous concentrations that underestimate CH₄ concentrations. This suggests the use of CC detectors are limited to samples adequately diluted with atmospheric air, at the surface, and interfacing with noninvasive, surface-based, sampling tools. This ensures sufficient O₂ supply to the sensor for complete combustion of hydrocarbons. Precautions are needed if a CC detector is used for soil probe subsurface measurements and/or conditions outside the recommended range of O₂ concentrations. For example, applications using the portable monitor for GM testing in subsurface environments requires safeguards to ensure accurate reporting, including a requirement to report O₂ concentrations. Multi-gas monitors in the industry are typically equipped with O₂ sensors, primarily for worker safety purposes, and such data can become part of reporting regulations. This will be especially relevant for subsurface measurements taken using invasive tools,

such as probes, for GM testing at abandoned well sites. Reporting the O₂ along with %LEL measurements will provide investigators, as well as regulators, with the site conditions at the testing location. O₂ measurements will verify the accuracy of CH₄ concentrations reported as well as confirm if a serious environmental or public/health hazard is present. Further testing is required to determine the impacts on linearity for a broader range of O₂ concentrations with respect to CC detection of CH₄. This would provide stakeholders and regulators with a better understanding of the threshold at which CH₄ measurements lose accuracy and become uninformative, based on the O₂ reported at the time of sampling.

To ensure the underestimated CH₄ concentrations were not the result of procedural errors, a quality check was completed with the gas bags to ensure minimal introduction of error in the calibration and measurement steps.

Table 2.5. Mid-range gas bag calibration test.

CH₄ Standard (ppm)	CH₄ Measured (ppm)	Percent error (%)
10,400	4,670	55
25,000	32,604	30
29,600	4,057	86

Calibration performed using mid-range standard containing 25,000 ppm of CH₄ with 12 %v/v O₂ supplied to portable monitor via a filled gas bag. Percent error calculated from certified CH₄ standard concentration.

Table 2.6. Mid-range DF regulator calibration test.

CH₄ Standard (ppm)	CH₄ Measured (ppm)	Percent error (%)
10,400	3,753	64
25,000	26,607	6
29,600	3,423	88

Calibration performed using mid-range standard containing 25,000 ppm of CH₄ with 12 %v/v O₂ supplied to portable monitor via a DF regulator (6 L/min). Percent error calculated from certified CH₄ standard concentration.

2.3.4 Quality check for calibration tests

To ensure the accuracy of CH₄ measurements reported in the calibration results, a quality check was performed on the gas bags. Gas bags are an integral part of the calibration procedure and are a likely source of air contamination during testing. Contamination can be introduced by tears in the bag material causing gas to be released, or when opening or closing the bag valves. Such issues would explain the profoundly underestimated concentrations and high errors (55-88%) in the calibration tests for the low- and high-range CH₄ standard measurements (Tables 2.5–6). A separate quality test was performed using 3-L gas bags. Quality testing was performed in the same fashion as the calibration test using the mid-range standard with the DF regulator; however, a subsample was taken for GC analysis prior to sampling all three standards in the 3-L bags using the portable monitor. Again, these measurements were performed in triplicate and averaged for reporting. Every replicate sample was subsampled and analyzed with the lab-based GC. Concentrations based on GC results are presented alongside portable monitor measurements to assess gas bag integrity (Table 2.7). Gas bags used in the calibration testing were also analyzed after testing was completed to ensure imperfections in bags did not introduce error.

Procedural testing using the 3-L gas bags resulted in CH₄ concentrations with a similar error to calibration results under the same conditions (Table 2.7). Gas bags containing the low- and high-range standards were underestimated by the portable monitor with errors of 67 and 87%, respectively; conversely, concentrations based on the GC analysis of the same three standard gases were closer to the certified concentrations with errors <10%. Portable monitor concentration measurements of the gas bag containing the mid-range standard were the most accurate (26,900 ppm vs. 25,000 ppm) with respect to the certified concentration and had a low percent error (8%). Hence, the GC results indicate minimal dilution of each CH₄ standard in the gas bags occurred, error within 10% of certified values, and confirm the gas bags were not the cause of the underestimates reported in calibration testing. Furthermore, GC sampling of 1-L gas bags, post-calibration testing, also resulted in concentrations close to GC results from the 3-L gas bags for the low-range (9,520 ppm), mid-range (23,740 ppm), and high-range (28,500 ppm) standards. As an addition to the quality check, O₂ was recorded during the calibration experiments and found to be absent and ruled out as a contributing factor. O₂ concentrations were consistently below detection limits (<0.1 %v/v), except for one experiment that had a concentration of 1,000 ppm (≥0.1 %v/v). This quantity was deemed to be within appropriate experimental error and within the uncertainty of the portable monitor O₂ measurements. Otherwise, O₂ detected by GC analysis were below the detection range of the portable monitor. The quality check confirms that the experimental results can be confidently interpreted and the design of the calibration experiments using gas bags is not a source of error.

Table 2.7. Validation check of gas bag composition using portable monitor and GC.

Standard Concentration	Portable monitor	Percent error	Lab-based GC	Percent error
<i>CH₄ (ppm)</i>	<i>CH₄ (ppm)</i>	(%)	<i>CH₄ (ppm)</i>	(%)
10,400	3,389	67	9,520	8
25,000	26,900	8	23,740	5
29,600	3,738	87	28,500	4

Calibration performed using mid-range standard containing 25,000 ppm of CH₄ with 12 %v/v O₂ supplied to portable monitor via a DF regulator (6 L/min). Percent error calculated from certified CH₄ standard concentration.

2.4 ‘Best practices’ for GM testing

2.4.1 Invasive sampling in GM testing

The comparison of surface-based and subsurface GM testing results suggests soil probes are more reliable than handheld monitors for identifying FGs at abandoned wells. Invasive tools, such as probes, are less susceptible to dilution by atmospheric gases as well as processes inhibiting gas migration to the surface (suppression). Sophisticated analytical equipment, such as a portable analyzer with an IR detector or GC-TCD, is identified as the best practice to determine accurate concentrations of soil gas CH₄ for GM testing. The application of portable monitors with CCD detectors in subsurface testing procedures requires additional precautions such as quality checks to ensure concentrations are not grossly underestimated. Important precautions identified in this study are as follows:

- Analysis of gases is restricted to surface applications to ensure the presence of the required concentration of O₂ for accurate detection of combustible hydrocarbons.

- Subsurface measurements (%LEL, %v/v, or ppm) should be reported with O₂ concentrations to allow accurate interpretation of GM testing results.
- Secondary equipment should be used to corroborate subsurface CH₄ concentrations measured by a portable monitor with a CC sensor.

2.4.2 *Limitations of portable monitor in GM testing*

This study suggests portable monitors can underestimate CH₄ concentrations under specific conditions and can impact their reliability with respect to identifying a GM issue. This conclusion supports a preliminary investigative report by BC regulators that notes portable monitors with LEL measurements are ineffective for detecting GM, along with visual signs of vegetative stress around the abandoned well site; instead, the report recommends the use of gas chambers or soil vapour surveys for GM testing.²⁸ The method highlighted in the report as the most effective indicator of a GM issue was to dispense water around the well centre and observe bubbling within the standing water.²⁸ However, this is not a practical approach and significant gas pressure is required to overcome the hydrostatic pressure of the water on surface. GM testing procedures in Saskatchewan take on reporting standards described in *Directive 20*.^{18,29} [REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

2.5 Conclusions and further work

Findings of this study compare sampling approaches with a focus on the accuracy of CC detectors that are commonly recommended by industry regulators for GM testing. The results indicate a disparity in detection of CH₄ when implementing the two most basic types of sampling approaches, dome or probe, in testing. Portable monitors show limited accuracy in probe sampling since soil gas measurements provide non-ideal O₂ concentrations (<10 % v/v) which are required for detecting CH₄. [REDACTED]

[REDACTED] Further work should be conducted to assess the validity of results presented in this study as well as O₂ threshold to determine the optimal concentration for accurate CH₄ measurements. Additional precautions need to be investigated when extending the application of CC sensors to ‘sour’ natural gas wells that contain H₂S, as gases containing sulfur species can foul the sensor and render the monitor inoperable.^{14,15}

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CHAPTER 3

DEVELOPING A MULTIVARIATE RISK ASSESSMENT TOOL TO DETECT GAS MIGRATIONS AT ABANDONED WELL SITES IN WESTERN CANADA

3.1 Introduction

Oil and gas (O&G) emissions constitute part of Canada's contributions to global greenhouse gases (GHGs).^{1,2} Within this sector, natural gas production and operational releases are sources of these emissions. Contributions (44%) to Canada's methane (CH₄) is thought to originate from practiced operations, fugitive releases, and decommissioned assets.^{1,2,3} Natural Resources Canada (NRCan) estimated in 2016 that roughly 5% of wells in Alberta emit fugitive gases (FGs).³ Of these wells, 30% were characterized as having serious emission flows, indicating an infrastructure integrity issue requiring remediation; the remaining assets produced non-serious flows.³ Of the serious flows, a small percentage (0.7%) of leaking wells contaminate the subsurface environment before reaching the soil surface.³ After the onset of regulatory monitoring in 1910, only 7% of the 25,000 of wells emitting FGs were identified as abandoned; this is comparable to estimates from Pennsylvania where 5–8% of CH₄ emissions are sourced to abandoned wells in the O&G sector.⁴ Estimates from the literature report 4.5–7.0% of carbon (CO₂) storage or enhanced oil recovery (EOR) wells in Alberta have developed well integrity issues, leading to FG emissions to the atmosphere⁵, and 14% of abandoned storage projects are estimated to develop FGs⁶. Along with these studies in Alberta, one completed in the UK indicates CH₄ emitted from abandoned assets, known to release FGs, presents higher flux rates than respective control sites.^{6,7} Estimates in these studies depend on open databases that rely on industry well monitoring and reports in this sector.^{3–5} In Alberta, databases are

provided by the Alberta Energy Regulator (AER); however, studies note discrepancies in reporting and logging categories/terminology, especially between historical and modern electronic datasets.^{4,6} Emissions estimates from Environment and Climate Change Canada's National Inventory Report do not designate fugitive sources of CH₄ and underestimate contributions from the natural gas sector due to the lack of tracing stray gases.^{3,7,8} Thus far in the literature, few studies specifically address unintended CH₄ releases (FGs) from abandoned wells in the natural gas sector. These assets provide an important opportunity to address Canada's Climate Action Plan with a specific focus on this sector to reduce CH₄ emissions by 2025.^{1,3}

Well integrity issues are identified as surface casing vent flow (SCVF) or soil gas migration (GM).^{9,10} The surface casing assembly protects adjacent formations/soils and potable aquifers from contamination.^{11,12} SCVFs from well integrity issues have the potential to unintentionally release GHGs into the atmosphere.^{3,11,12} SCVF testing aims to detect gases that arise from a well integrity issue by measuring flow rates of gases that have escaped from production tubing and into the SCV assembly.^{9,10,11} Soil GM typically refers to gases migrating to the surface outside of the SCV assembly. Regulatory GM testing is required for early identification of well integrity issues to prevent FG releases into the environment from SCVs and through soils.^{3,7,13} Both SCVF and GM testing procedures are completed throughout a well's lifecycle and are an important step in decommissioning a well.^{9,10} The regulatory classification of a serious GM issue is determined based on its potential to be a public or environmental (groundwater contamination) hazard.^{10,12,13}

GM issues can arise from well integrity issues during initial completion of a well or at any point of the production life cycle of an energy asset.⁵ Well abandonment and land reclamation ultimately result in a cut and capped well.^{5-7,12} Once the well is buried and the land reclaimed, the production annulus and SCV are no longer accessible. Hence, soil GM testing is primarily utilized to identify FGs at an abandoned well site and to assess well sites for GM issues. In studies of reported GM issues, quantities of FGs are determined from a mix of active and abandoned wells, and few reports thus far specifically address CH₄ releases from abandoned natural gas wells through GM testing.^{4-7,11,12}

GM testing guidelines provided by the AER outline recommendations for procedures, equipment, and methodology to detect FGs at active and abandoned wells.^{9,10} Recommendations for testing procedures indicate subsurface sampling at a depth of 50 cm, with sampling locations placed radially at intervals of 1 or 2 m surrounding the well center.⁹ In practice, measurements are often limited to 30-cm depths to accommodate ground disturbance regulations for routine monitoring.¹⁰ In practice, GM monitoring is completed using either noninvasive, surface measurements or invasive, subsurface (soil gas) measurements; however, a study from Pennsylvania suggests site gases are underestimated by 13% when measuring at the surface.^{6,7,12} Soil GM testing using subsurface techniques, such as probes, can introduce additional complexities, including the atmosphere, natural biological CH₄ (biogenic), or microbiological degradation of CH₄ (CH₄ oxidation).¹³⁻¹⁷ These factors can produce conflicting results and make the interpretation of GM test results more complicated.

Geochemical GM identification approaches use a combination of concentration-dependent and concentration-independent techniques. Concentration-dependent techniques are based on the compositional characterization of soil gases and often focus on CH₄, ethane (C₂H₆), and propane (C₃H₈), along with larger hydrocarbon chains. This approach is often limited because of various types of contamination from the atmosphere (O₂, N₂) and natural environmental sources of biogenic gases.^{3,12} Concentration-independent techniques improve source identification as they can often be used to distinguish biogenic from thermogenic sources using stable isotopes.^{3,12,14–21} Thermogenic production zone gases often have isotopic compositions of CH₄ that contains higher concentrations (enriched) of the heavier carbon isotope (¹³C) over the lighter (¹²C), relative to biogenic gases.^{19–21} Stable isotope measurements are reported using delta notation (δ) based on the ratio of the heavier isotope over the lighter (¹³C/¹²C, ²H/¹H).²² Source identification of CH₄ often utilizes a combination of δ¹³C-CH₄ and δ²H-CH₄ because thermogenic gases can have considerable overlap with natural biogenic CH₄.^{17,19–20,21} Literature values for δ¹³C-CO₂ are not prevalent for thermogenic sources due to its absence in the composition in natural gas profiles; however, measurement of this isotope becomes important when additional bacterial pathways in the soil interact with migrating gases.^{14–17} Thus, concentration-independent indicators (stable isotopes) often require concentration-dependent indicators (soil gas composition) to identify contamination sources based on relative volumes of gaseous species in a sample. Likewise, concentration-dependent indicators require independent indicators to trace stray gases to their origin to accurately confirm a GM issue at an abandoned well site. In practice, identification of

a GM issue often depends on a single sample, or limited sample-to-sample interpretation from GM test results.^{3,10} Utilization of a small sample set can either miss a GM issue due to limited sampling around the well centre or from environmental interactions that contaminate soil gases and confound interpretations.

Geochemical approaches to identify gas sources often use classic graphical representations and linear modelling techniques.^{4-7,12,16-18} These approaches compare field site composition and stable isotope data to categorize field samples based on different types of reference samples (production zones in the region). The insight gained from such crossplots is identification of gas samples characteristic of production zone (thermogenic) gases, containing higher concentration of C₂₊ species, and microbial gases, which typically do not contain longer chain hydrocarbons.^{12,16} Interpretation of isotope data in GM testing often utilizes Schoell or Whiticar style plots.¹⁹⁻²¹ These plots present isotopic sources in specific regions of the graph, and overlaying these regions with data points can identify the most likely source of each sample (Figure 1.3).^{12,18-21} Schoell plots often analyze gas composition with isotopes to identify probable concentration trends.^{16,18} Approaches to risk assessment that utilize cross or Schoell style plots are only capable of analyzing one trend at a time. Interpretations from graph to graph can be misleading when a collective, multi-variable approach is required to differentiate between sources (e.g., CH₄, and C₂₊), while accounting for possible interferences from the environment (CO₂, O₂, and N₂). This becomes arduous as commercial laboratories provide GM datasets containing multiple geochemical tracers for a single sample of soil gas.^{12,20,23-24} Distinction between background and thermogenic gases has been achieved through averaging site

gases at control sites and using standard deviations from mean gas constituents to determine thresholds for elevated or naturally occurring CH₄.¹² Furthermore, the use of average gas concentrations at specific well locations has been integrated with statistical testing. Analysis of variance (ANOVA) has been used to compare active production wells with control sites to determine sites with significant emissions, along with environmental or site factors that may play an important role with respect to FGs.⁷ Hence, this study presents a multivariate statistical and mathematical approach to capture environmental interactions that impact soil gases to interpret the status of an abandoned well site in Western Canada.

Mathematical and statistical tools are often applied within the field of environmental forensics to model or source contaminants.²³⁻²⁴ One common exploratory tool to normalize and reduce complex, high-dimensional datasets is principal component analysis (PCA).²³⁻²⁶ PCA in its simplest definition reduces complex, high-dimensional data and projects datasets with multiple variables (soil gas constituents) into a simplified frame for interpretation.^{23,23-26} The newly projected data are plotted against uncorrelated axes that retain a percentage of the variability, or character, of the original dataset.²⁶ Using two or more of these axes or principal components (PCs) facilitates interpretations compared to high-dimensional data that cannot be visualized on a single scatter plot. An advantage of PCA is filtering out data redundancy caused by natural background, or noise, to bring out latent characteristics of the dataset.²³⁻²⁶ An underlying assumption of PCA is that all variables, or soil gases, in the model are linearly correlated; nonlinear trends or data clusters are not accounted for.²³⁻²⁶ However, improvements have been made to work

around the linearity assumption.²⁶ With hierarchical clustering tools, analysis of data clusters can be performed post-PCA modelling to group highly correlated data points (sampling locations).²⁷ Clustering tools group data points using mathematical calculations based on the distance between two data points.²⁷

[REDACTED]

[REDACTED] [REDACTED] [REDACTED] [REDACTED] After dimension reduction, data clustering was performed using K-means, allowing for a more insightful and accelerated risk assessment of GM data. An additional contribution from this study offers is an evaluation of recommended field practices without standardized testing and reporting procedures. In place, we offer strategies that could avoid false negatives and/or false

positives to ensure risk assessment accuracy at abandoned well sites in Western Canada.

3.2 Materials and methods

3.2.1 Field site map

Gas migration sample point locations

[REDACTED]

3.2.2 Soil gas collection

[REDACTED]

[REDACTED]

[REDACTED] Probes were equilibrated for >1 h before sampling. Two samples were collected from the excavated well centre at this location after GM testing for source characterization. Gases were sampled with a 60-mL gas-tight syringe then transferred to a sterile, evacuated 60-mL serum vial.

Soil gas locations in the 2019 field program (Figure B.3) were sampled using soil push probes at 30 cm depths at 20 different point locations over 2 d (Figure A.2). Each location was left to stabilize for >1 h. Soil gas was initially sampled using a 60-mL gas-tight syringe with a three-way luer-lock valve to prevent contamination in between sample collection. Gases collected on site were stored in 60-mL sterile and evacuated serum vials (Wheaton Glass).

3.2.3 Soil gas analysis

Soil probe gas samples from the 2014 field program were analyzed for composition and stable isotopes at the University of Calgary. Soil gas samples stored in serum bottles in 2019 were analyzed at the University of Windsor. Gas samples

collected from the field were analyzed on an Agilent 7890B gas chromatograph (GC) equipped with a flame ionization detector (FID) to quantify hydrocarbons (CH₄, C₂H₆, and C₃H₈) and a thermal conductivity detector (TCD) for CO₂, and N₂, O₂. Samples from 2019 processed for stable carbon isotopes ($\delta^{13}\text{C}$) were analyzed on a Thermo Trace 1310 GC interfaced with an Isolink III connected to a Delta V Plus isotope ratio mass spectrometer (GC-IRMS). Stable hydrogen isotopes ($\delta^2\text{H}$) were analyzed on a Thermo Trace Ultra GC interfaced with an Isolink connected to a Delta XP IRMS (GC-IRMS).

Analytical error in reported $\delta^{13}\text{C}$ values is 0.5‰ and $\delta^2\text{H}$ values is 5‰. Uncertainty in reported soil gas concentrations is 5% of chromatograph peak area.

3.2.4 PCA modelling of soil gas data

PCA was used to identify correlated geochemical tracers in soil gas data. Soil gas composition and stable isotopes were treated separately to ensure optimal sample sizes for interpretation and statistical testing, but also to respect unit/metric differences. Prior to analysis, data were standardized by taking the root mean square of the gas concentrations and stable isotopes. Selection of meaningful PC axes for data visualization was determined when cumulative percent variance of axes was $\geq 95\%$.²³ When discrepancies with respect to axis selection arose, a *scree test* was used to identify axes retained percent variance when the cumulative variance was lower (90% lowest) than 95%.^{23,26} This ensured that the axes retained contributed to data interpretation and were not due to random error. Significant soil gas components and stable isotopes were determined by taking the absolute value of their respective loading score. The absolute value of loading scores ≥ 0.75 for soil gas composition or

stable isotopes were considered significant and values between 0.50 and 0.75 considered moderately significant.²³ PCA was performed using the *prcomp* function in *R* statistical software.²⁸

3.2.5 Clustering method

Clustering of data points was completed with the selected principal components from the gas component and stable isotope PCA modelling. Data cluster centers (centroids) for K-means clustering were predetermined by partitioning around medoids (PAM). PAM searches the dataset for *k* representative objects, or medoids, to ensure the minimal total distance between data points and medoids is achieved, with adjustment of the number of medoids, or cluster centers, as needed. Once the lowest sum is achieved, the medoids, or cluster centers, are used as centroids in clustering data points with K-means. A second clustering method was applied because the K-means algorithm (Euclidean distance) provided more informative groupings of data in this study. Clustering was performed using the *fpc* package in *R* statistical software.^{28,29}

3.2.6 Sample size dependency

Determination of sample size dependency was completed using Fisher's exact test (a variation of the chi-square (χ^2) statistical test of independence) used for small sample frequencies.³⁰ Once clustered groups were identified, sample size distributions of categorized soil gas compositions and isotopes were compared to total sample size (*N*) and computed as a ratio or frequency using a contingency table.³⁰ Significance testing ($\alpha = 0.05$) was completed between observed source gas, or 'hotspot', frequency and hypothetical hotspot frequency. Independence testing of observed

locations can predict sample ratios that could be detected at an abandoned well site with a known active GM (AGM). Fisher's exact test was performed using *R* statistical software.²⁸

3.2.7 Sources of error

Assigning significance to PCA variables warrants caution due to the small sample sizes used in modelling. Hence, datasets were combined and modelled to ensure proper significance association within GM testing variables. Additionally, quantification limits constrained the detection of gas components. These components should be perceived with caution due to concentrations below detection limit (BDL) or their small contributions compared to other measured constituents.

3.3 Site GM testing history

[REDACTED]

[REDACTED]

[REDACTED]

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3.4 Results and Discussion

3.4.1 PCA of soil gas constituents

Multivariate analysis of soil gases included six gas constituents (CH_4 (C_1), C_2H_6 (C_2), C_3H_8 (C_3), N_2 , CO_2 , and O_2) that were measured from locations collected around the abandoned well. Output of dimension reduction for 2014 (Figure 3.2) and 2019 (Figure 3.3) identified two meaningful axes, providing a 2D representation that best approximates the 6-dimensional (6D) scatter plot of all constituents. Samples taken around the well centre are presented as data points (Figures 3.2–4) with gas species as variable markers or arrows. A combined analysis was completed to interpret differences between GM tests (Figure 3.4)

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED] PC1 contributed to 81% of the variance in soil gas composition in 2014. Hydrocarbon compositions appears to be correlated more strongly along PC1, which represents a correlated [REDACTED] group of variables [REDACTED] with a uniform, unidirectional influence (Table E.3).²⁶ The [REDACTED] group, CO_2 , and O_2 are not correlated together. The [REDACTED] group and N_2 are oppositely correlated, as well as CO_2 and O_2 . The relationship along

the horizontal axis is stronger for the [REDACTED] group and N₂ compared to CO₂ and O₂, which likely demonstrates the influence of mixing with atmospheric gases introduced during the sampling process. The weaker relationship of [REDACTED] and N₂ along the vertical axis suggests a potential difference between the CO₂ and O₂ sources. Similar trends are noted in the 2019 data (Table E.5), where ordering of gas component loadings, from least to greatest, along PC1 axis is [REDACTED], and [REDACTED] (Table E.6). Gas components along the PC2 axis from least to greatest, [REDACTED] [REDACTED] (Table E.7). In this case, the stronger horizontal axis also shows the CO₂ highly correlated with the hydrocarbon group which are oppositely correlated by O₂ and N₂. This suggests a stronger relationship between both the hydrocarbon group and CO₂ as well as O₂ and N₂. Atmospheric gases are more strongly correlated with the PC1 axis (Figure 3.3) than observed in 2014 (Figure 3.2), which may indicate the variability of the original dataset could be influenced more by these gases. Additionally, data spread appears to be concentrated more horizontally than the vertical spread observed in 2014. [REDACTED]

[REDACTED] Gas composition ordering along PC2 supports this finding. In the 2014 data, CO₂ and O₂ loadings are the two highest influential gas components along PC2; however, in 2019 these gases are in the last three components of influence along this axis (Figure 3.3). Hence, more variability (84%) is attributed to gases influenced by [REDACTED] composition, which again may indicate elevated levels of CH₄ and other [REDACTED] that are greater than natural background.

PCA models demonstrate that a large portion of the variability in the soil gas data is likely attributed to atmospheric gases diluting the hydrocarbon and CO₂ composition of subsurface gases. Procedurally, this could be from contamination when submerging the soil probes and/or insufficient purging of a sample point location, and/or insufficient soil gas flux rate to displace the atmospheric contamination. The orthogonal relationship between some of the arrows (gas components), although slightly less orthogonal in the 2019 model (Figure 3.3), suggests the hydrocarbon group is not strongly correlated with CO₂. This is supported by the absence of CO₂ in the GM source gas in the subsurface, suggesting the relationship between CH₄ and CO₂ observed in the PCA may be indicative of the biodegradation of CH₄ as the source of CO₂ at this location. Arguably, data spread appears to be equally horizontal and vertical; however, the horizontal axis (PC1) has the dominant descriptive power.

Another explanation for these results may be due to small sample size and possible outliers present in the GM datasets. The variance and the visual data spread in Figure 3.2 may be skewed due to inclusion of samples with considerable degraded organic matter, which produced the more concentrated data points horizontally in the PCA biplot for 2019 (Figure 3.3). Along the second axis, C₃ presents a potential correlation with other hydrocarbon gases, as observed in 2014 (Figure 3.2). This difference may be due to the low detectability of C₃ during this investigation, which most likely resulted in the significance of this variable and the lower correlation to other gas components in the PCA model (Table E.7). To properly compare

compositional distribution correlations between GM tests, both datasets were merged and modelled with PCA (Figure 3.4).

Collectively analyzing samples taken around the well centre from both GM tests (Figure 3.4) produced modelling results similar to 2014 (Table E.8). No moderate significance or significant gas components were identified along the PC1 axis (Table E.9); however, influence in data spread from least to greatest loadings for gas components is [REDACTED]. Along PC2, gas components that are influential to data spread, from least to greatest loadings, are [REDACTED] and CO₂. Moderate significance (Table E.10) was identified for CO₂ and O₂, which aligns with the PCA from 2014 and provides more clarity with respect to the 2019 results. Overall, the distribution of soil gas samples collected at this location indicates two different correlation influences for 2014 and 2019 causing two distinctly different distribution patterns (Figure 3.4). This could indicate a greater influence of [REDACTED] in 2019 compared to 2014.

Measurement of soil gases during GM testing occurred at different depths in the two years. Soil probes in 2019 were uniform and only reached 30 cm into the subsurface, whereas in 2014 sampling depths ranged from 50 to 200 cm. Deeper soil measurements likely resulted in greater influence from biological degradation compared to shallow measurements, which may also have introduced relatively greater atmospheric contamination, depending on installation and purging methods. Variation in depth measurements most likely introduced greater data spread in 2014, whereas depth measurements consistent at 30 cm in 2019 present a more uniform data spread. Regardless, PCA modeling of six gas components confirms the concentration-

dependency of gas components, where contamination of site gases plays a very complex role and affects the interpretation and GM risk assessment. To further understand these complexities, modelling was also applied to stable isotope measurements analyzed in each GM test.

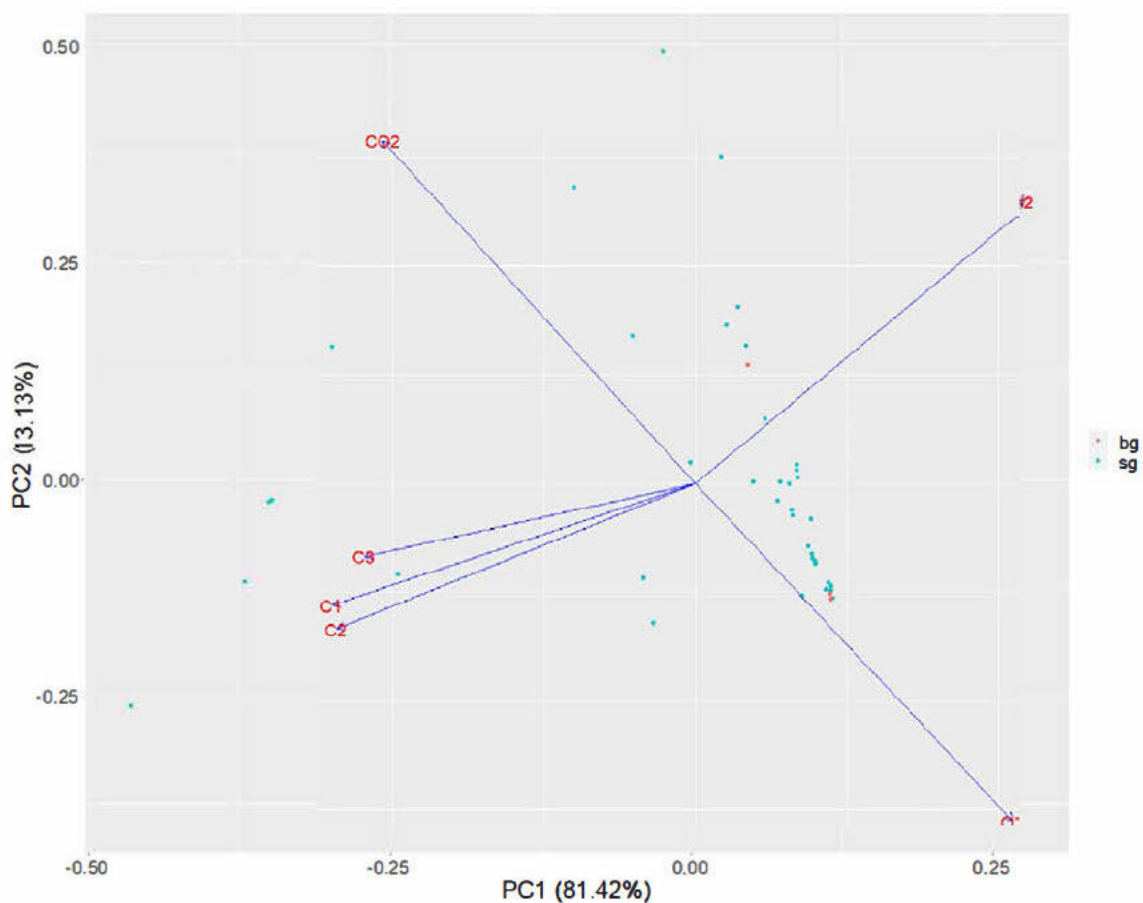


Figure 3.2. Biplot for 2014 soil gas composition taken around the abandoned well site. Data points present background (bg) samples as light red circles and soil (sg) samples as light blue circles. Percent variance retained along each axis indicated in brackets.

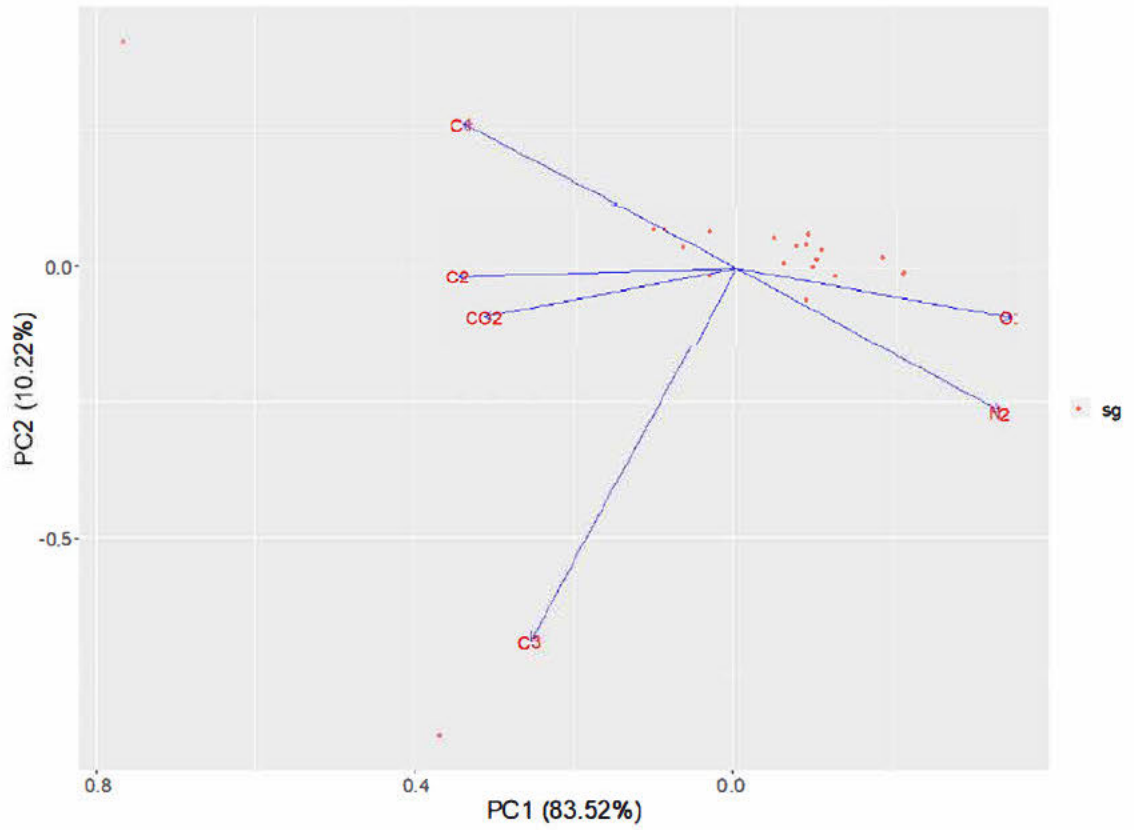


Figure 3.3. Biplot for 2019 soil gas composition taken around the abandoned well site. Data points present soil (sg) samples as light red circles. Percent variance retained along each axis indicated in brackets.

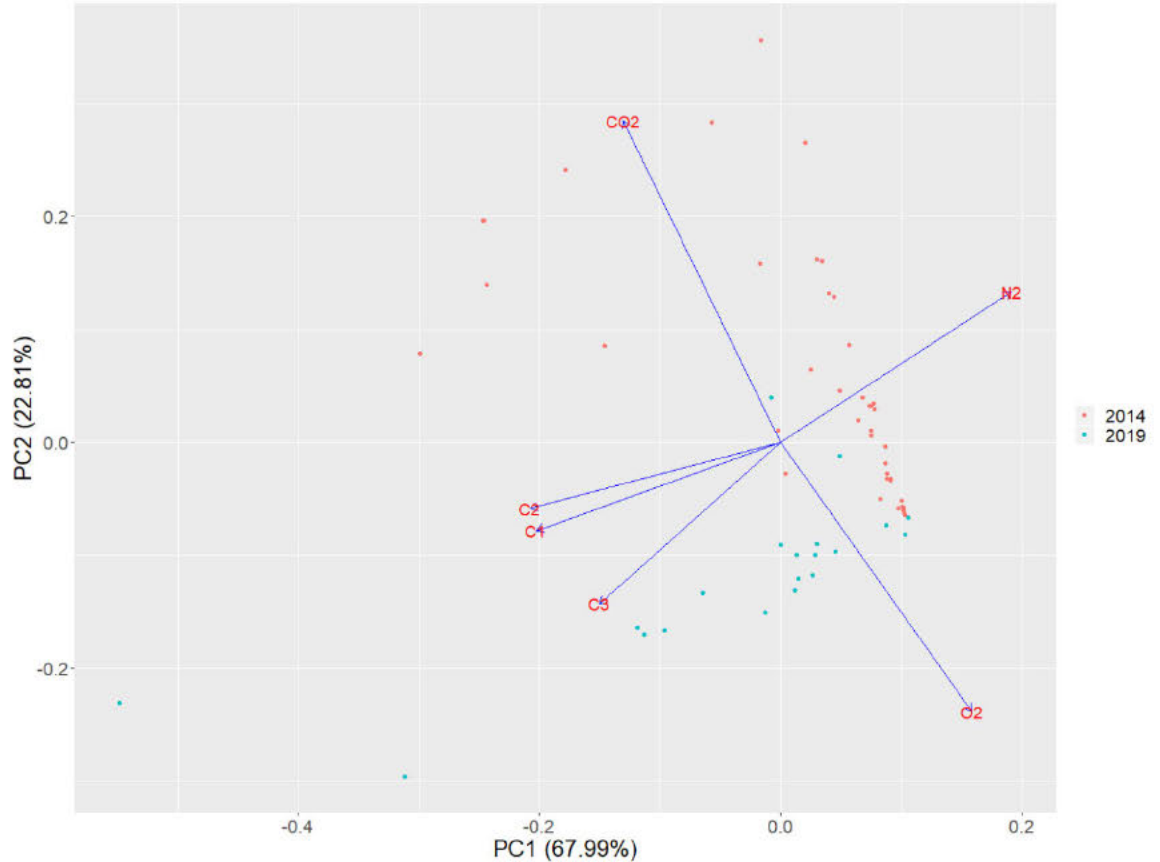


Figure 3.4. Biplot for combined soil gas composition taken around the abandoned well site. Data points from 2014 shown as light red circles and 2019 as light blue circles. Percent variance retained along each axis indicated in brackets.

3.4.2 PCA of soil gas stable isotopes

Modelling of soil gas stable isotopes in 2014 and 2019 included three different compound specific stable isotopes ($\delta^{13}\text{C-CH}_4$, $\delta^{13}\text{C-CO}_2$, and $\delta^2\text{H-CH}_4$). Dimension reduction of stable isotope datasets identified two meaningful PC axes in 2014 (Figure 3.5) and 2019 (Figure 3.6), resulting in a 2D representation of the original 3-dimensional (3D) scatter plot of isotope tracers. Samples taken around the well centre are presented as data points for 2014 (Figure 3.5) and 2019 (Figure 3.6), while stable isotopes are shown as variable markers or arrows. Stable isotope analyses were not conducted for all locations analyzed for soil gas composition, so PCA biplot data distributions are limited due to select locations around the well centre. A combined

analysis (Figure 3.7) was completed on stable isotopes from both GM tests to identify differences between isotope distributions.

Results from samples in 2014 retained 97% of the variance in the original dataset and show sparse distribution due to the small sample size (Figure 3.5 and Table E.11); however, loadings of stable isotopes along PC1 axis indicate the greater influence of CH₄ isotopes, with moderate significance, and with $\delta^{13}\text{C-CH}_4$ being more influential than $\delta^2\text{H-CH}_4$ (Table E.12). CH₄ isotopes ($\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$) show stronger correlation with the PC1 axis and are highly correlated tracers. Conversely, PC2 is more strongly correlated with the CO₂ tracer ($\delta^{13}\text{C-CO}_2$), with a significant loading score along this axis, followed by $\delta^2\text{H-CH}_4$ and $\delta^{13}\text{C-CH}_4$ (Table E.13). The greater variance of the dataset along PC1 (69%) is attributed to CH₄ and may indicate [REDACTED] background or degraded matter in the soil. Comparatively, PC2 captures less variation (27%) and could affirm the secondary interaction in PCA biplots of gas compositions. CH₄ oxidation is known to impact tracers, where $\delta^{13}\text{C-CH}_4$ becomes more positive (enriched in ¹³C) and $\delta^{13}\text{C-CO}_2$ more negative (depleted in ¹³C), which could explain the vertical data point spread. Due to small sample size, these are only speculations. A better description of stable isotopes at this abandoned well would require a larger sample size along with isotopic characterization of background measurements, which did not occur in either GM test.

Modelling results for 2019 (Figure 3.6) stable isotopes of soil gases are identical to correlations from 2014 (Figure 3.5). The 2D representation captured 98% of the original dataset variance (Table E.14). Isotope loadings were, again, moderately

significant for CH₄ tracers along PC1 and significant for CO₂ along PC2 (Table E.15–16). CH₄ tracers are more highly correlated with PC1, as well as more strongly correlated to each other, whereas the CO₂ isotope tracer shows a stronger correlation with PC2. Stable isotope data spread appears to be more restricted to the horizontal direction along PC1, accounting for 66% of data variance (Table E.14). Compared to 2014, data scatter influence appears to be less in the vertical direction along PC2, accounting for 32% of the data variance. However, this may be due to a larger sample size in this dataset, which essentially ‘filled-in’ the distribution sparseness noted in 2014. Another interpretation is that less oxidation of CH₄ caused the data distribution to be more concentrated due to more consistent values for $\delta^{13}\text{C-CH}_4$ and subsequently values of $\delta^{13}\text{C-CO}_2$. This distribution differences between 2014 and 2019 was also noted in the composition biplot scatter (Figure 3.2–3). Data spread could also indicate a stronger influence [REDACTED] on isotopic character than the background or degraded organic matter. All samples (excluding one with a very low concentration) in the PCA composition biplot (Figure 3.2–3) were analyzed for stable isotopes; however, even with the increase in data points the distribution is scattered and may include outliers. To clarify differences and confirm source influences in GM test results, a PCA model was generated using both 2014 and 2019 stable isotope measurements (Figure 3.7).

Combined PCA analysis of 2014 and 2019 stable isotopes (Figure 3.7) gives results congruent with separate PCA results in 2014 (Figure 3.5) and 2019 (Figure 3.6). Isotope loadings were consistent throughout each investigation as well as in the combined analysis (Table E.17). PC1 axis loadings, from least to greatest, are $\delta^{13}\text{C-}$

CO₂, δ²H-CH₄, and δ¹³C-CH₄ (Table E.18) while loadings along PC2, from least to greatest, are in the reverse order (Table E.19). All plots (Figures 3.5–7) demonstrate moderate significance for δ¹³C-CH₄ and δ²H-CH₄ along the PC1 axis, accounting for 65% of the data variance (Table E.17–19). The PC2 axis is significantly correlated with δ¹³C-CO₂ and accounts for 31% of the data variance. The total variance captured by stable isotopes is 95% and clearly presents two different data distributions for 2014 and 2019 GM results. The combined stable isotopes model presents 2014 sample locations with a more vertically spread compared to 2019. Hence, there is less correlation of 2019 sample locations to δ¹³C-CO₂. This could indicate fewer biological interactions, CH₄ oxidation or degraded organic matter, and thus reduced variability in stable isotope distribution when compared to 2014 (Figure 3.5). Along with the shift observed in soil gas composition, stable isotopes also could indicate a shift ■■■■■ in the soil at this abandoned well site. ■■■■■

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■■■■■ Overall, PCA results are only descriptive at this point and cannot be used to definitively conclude gas composition or stable isotope trends or a shift ■■■■■ from 2014 to 5 years later.²⁶ Thus, a post-processing technique (K-means) was required to inform the descriptions outlined above.

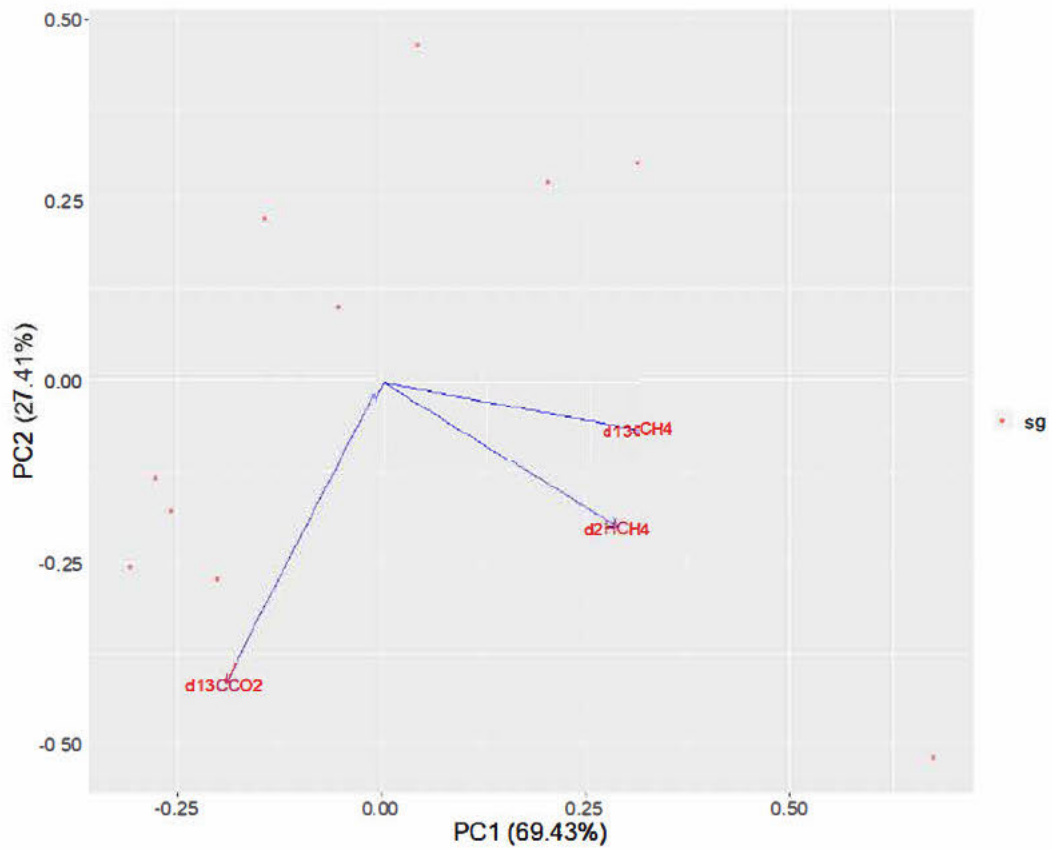


Figure 3.5. Biplot for 2014 soil gas stable isotopes taken around the abandoned well site. Data points present soil gas (sg) samples as light red circles. Percent variance retained along each axis indicated in brackets.

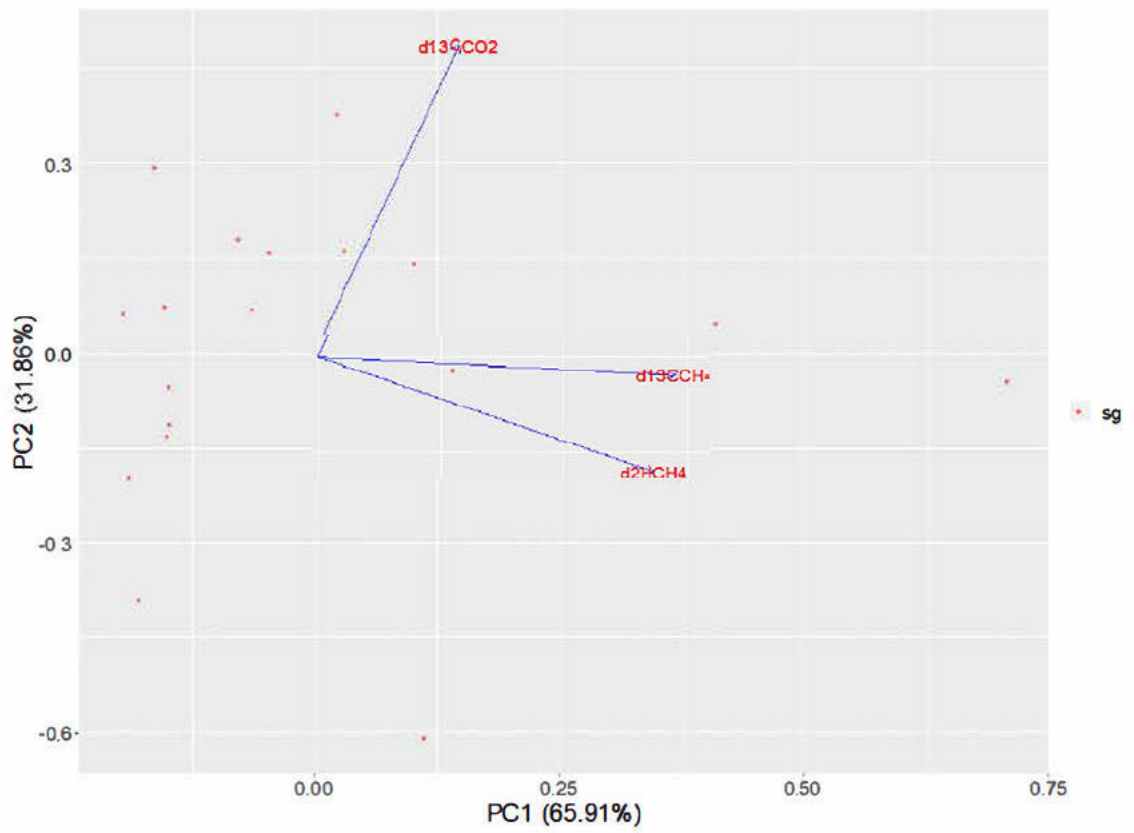


Figure 3.6. Biplot for 2019 soil gas stable isotopes taken around the abandoned well site. Data points present soil (sg) samples as light red circles. Percent variance retained along each axis indicated in brackets.

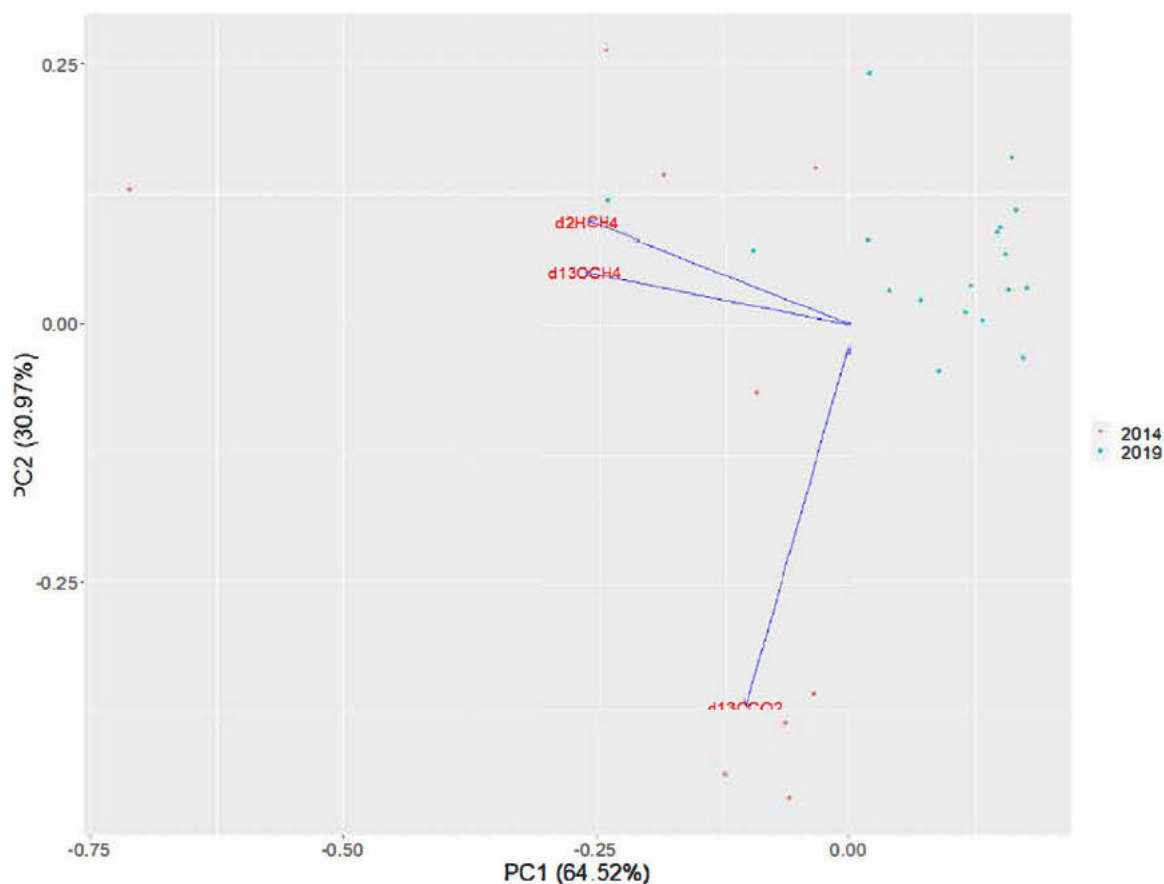


Figure 3.7. Biplot for combined soil gas stable isotopes taken around the abandoned well site. Data points from 2014 shown as light red circles and 2019 as light blue circles. Percent variance retained along each axis indicated in brackets.

3.4.3 Groups characterized by soil gas composition

Utilizing PCA models generated from site soil gas compositions, a hierarchical clustering method (PAM) was applied to calculate optimal cluster centres (medoids) and then subsequently use the number of selected centres to group data points with K-means clustering. Results from the clustering analysis indicate two cluster centres and therefore two chemically distinct groupings of soil gas samples within the 2014 and 2019 GM datasets (Figures 3.8-9). These centres were then used to group data points (samples) in respective PCA biplots. The samples in a given group were then averaged and the source identified from background samples included throughout the PCA modelling. XXXXXXXXXX characterization was determined using a source gas

sample collected in 2014 that returned a source gas composition of [REDACTED], respectively. Background (baseline) measurements were collected in the 2014 GM test (Figure 3.2) and subsequently used to confirm groupings of compositional sources (Table 3.1). The background group observed in 2019 (Table 3.2) was later confirmed by clustering the combined model of soil gas composition (Figure 3.10).

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED] Contamination by atmosphere, oxidation, or degraded organic matter in the soil are other likely possibilities related to the elevated levels of CO₂, O₂, and N₂ observed in field soil gas samples (Tables 3.1–3). [REDACTED]

[REDACTED]

[REDACTED]

[REDACTED] [REDACTED] [REDACTED]

[REDACTED]

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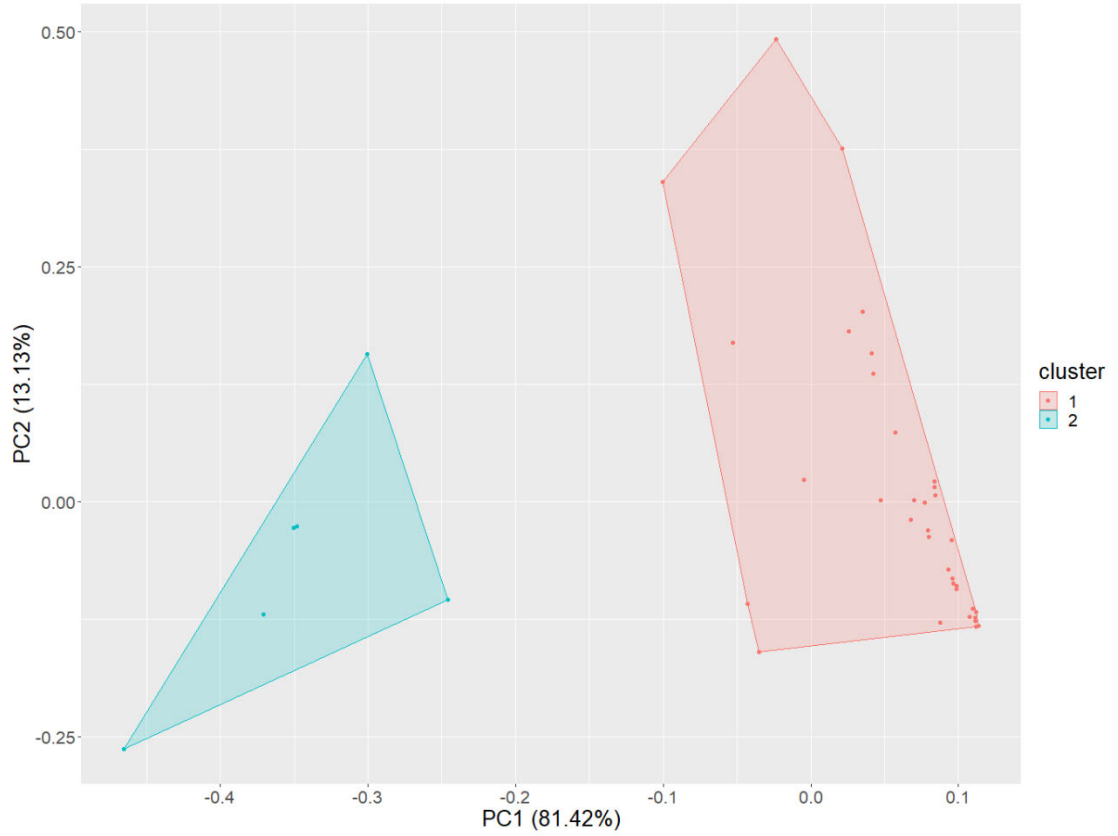
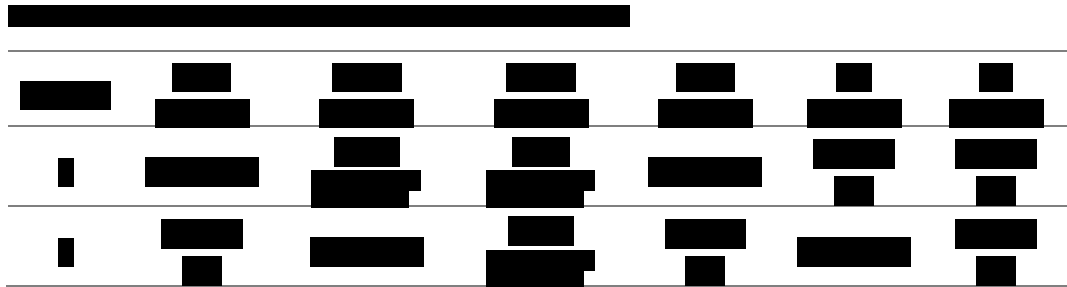


Figure 3.8. K-means clusters of 2014 soil gas composition biplot. [REDACTED] Percent variance retained along each axis indicated in brackets.



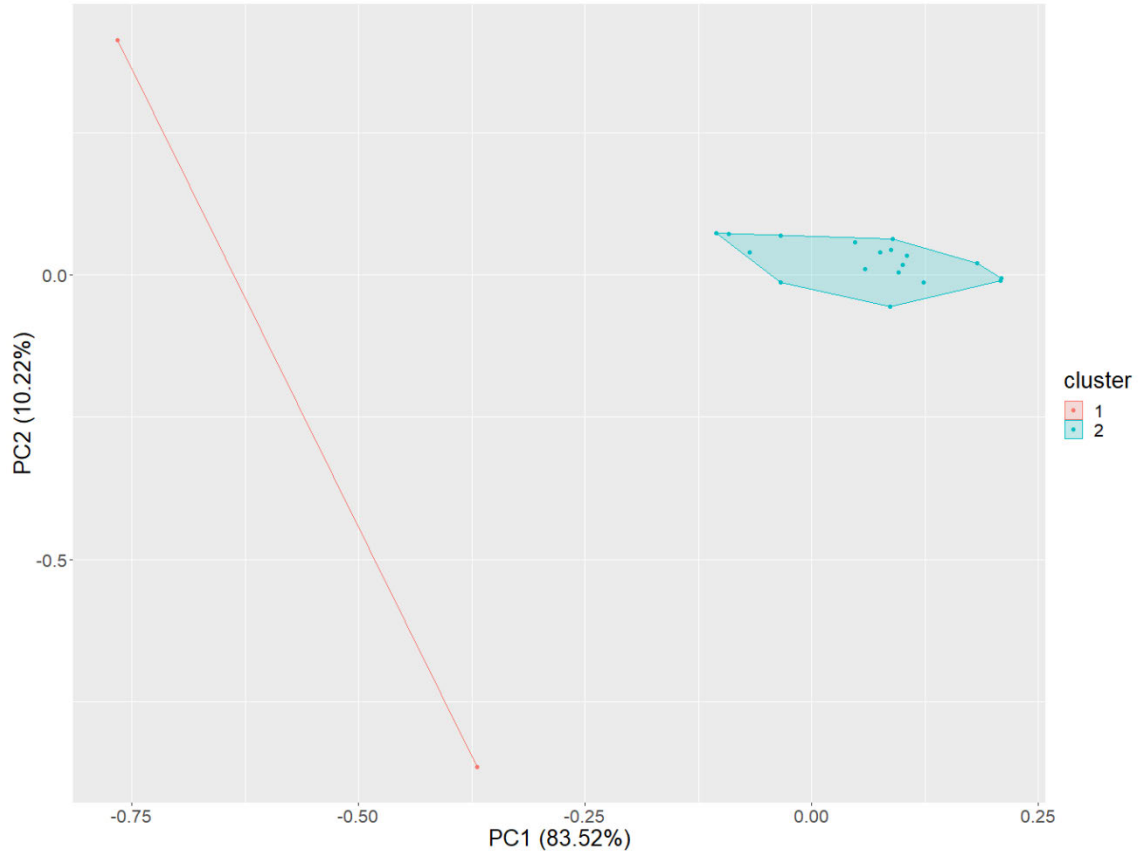


Figure 3.9. K-means clusters of 2019 soil gas composition biplot. [REDACTED] Percent variance retained along each axis indicated in brackets.



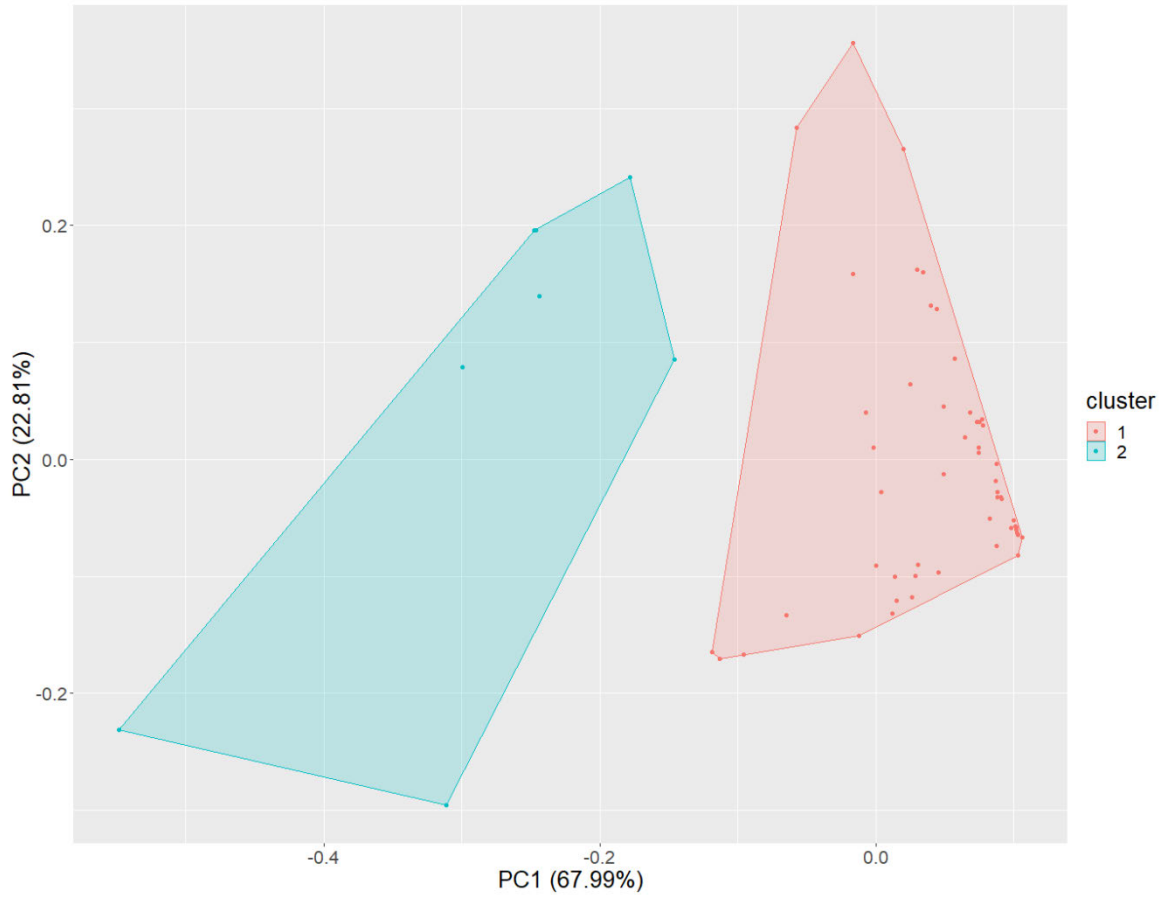


Figure 3.10. K-means clusters of combined soil gas composition biplot. ██████████ Percent variance retained along each axis indicated in brackets.



3.4.4 Groups characterized by soil gas isotopes



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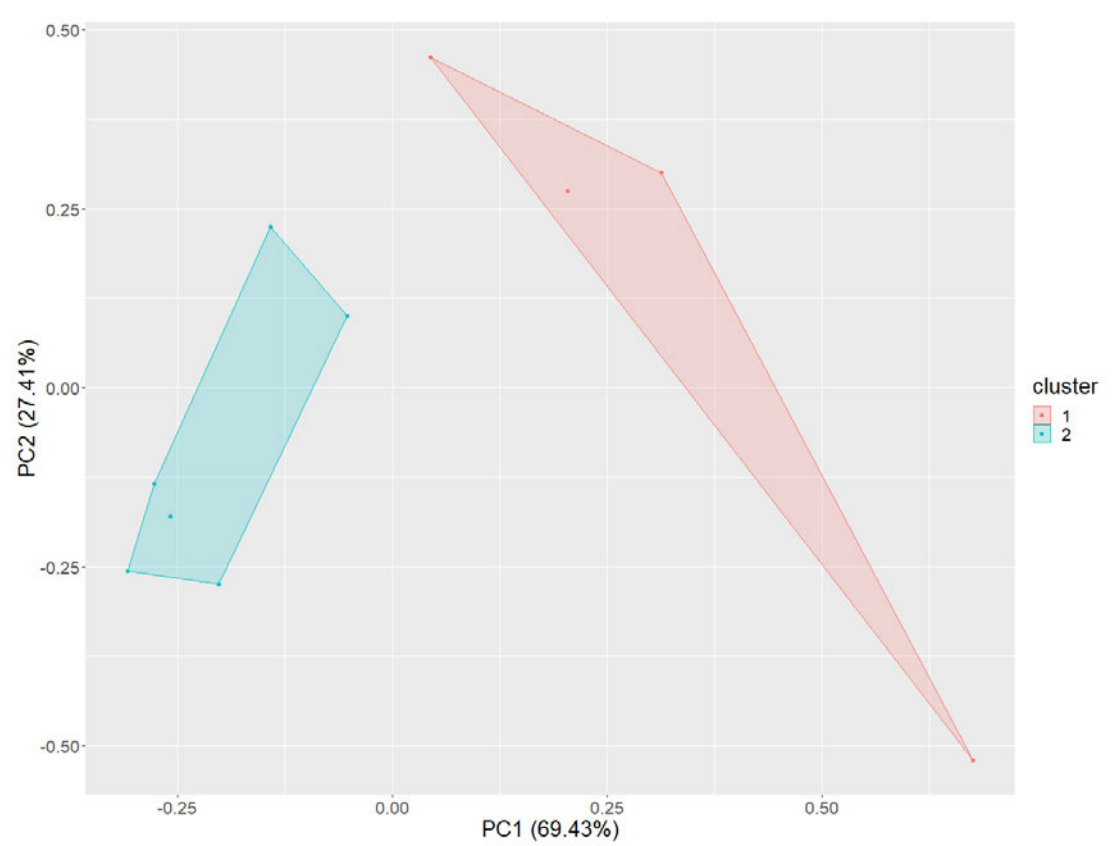


Figure 3.11. K-means clusters of 2014 soil gas stable isotopes biplot. [REDACTED] Percent variance retained along each axis indicated in brackets.

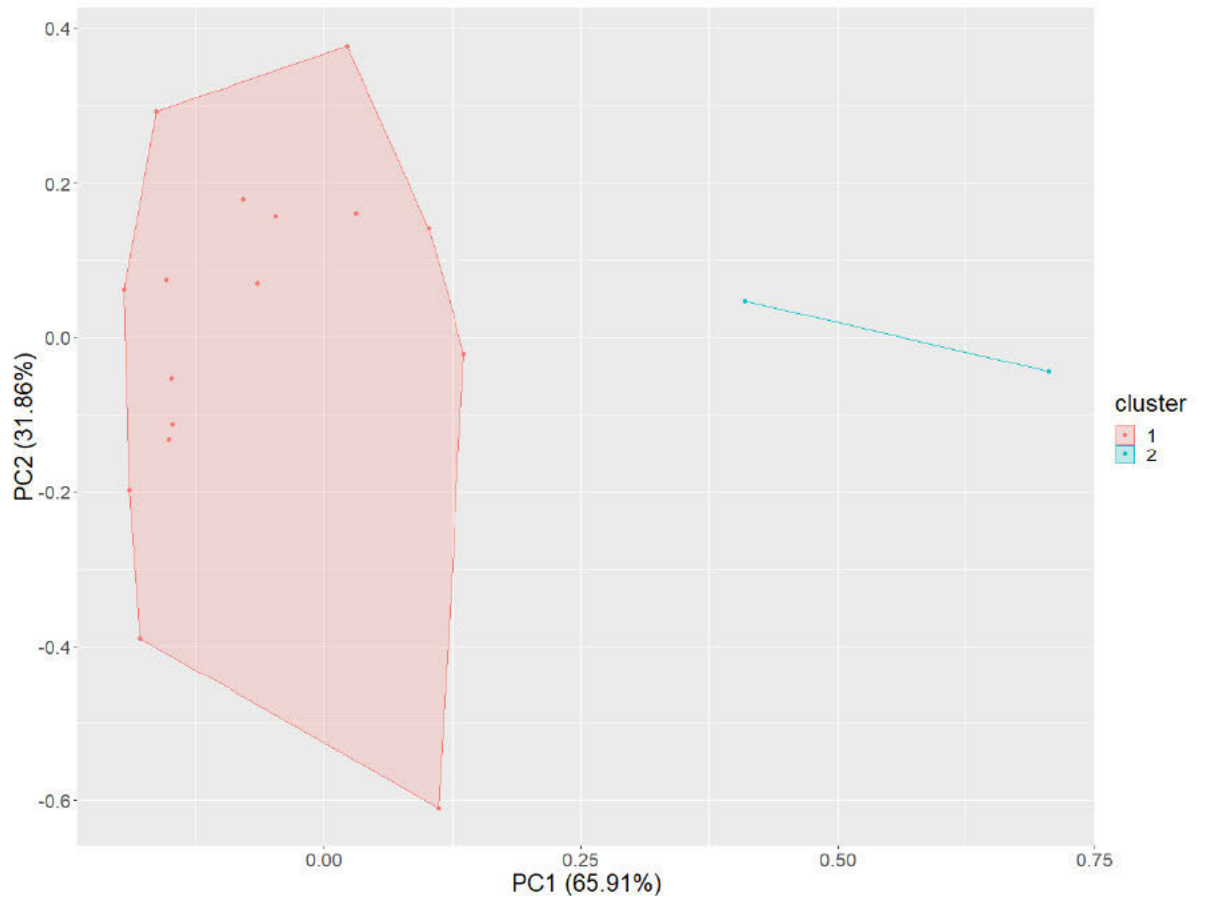


Figure 3.12. K-means clusters of 2019 soil stable isotopes biplot. [redacted] Percent variance retained along each axis indicated in brackets.





Figure 3.13. K-means clusters of combined soil gas stable isotopes biplot. [REDACTED]
 [REDACTED] Percent variance retained along each axis indicated in brackets.

[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]

3.4.5 Predicting sample sizes for GM testing

A Fisher's exact test was utilized to determine the most effective sample size, and possibly sampling pattern for GM testing, at an abandoned well with a known GM issue and the same geological background. Statistical testing was applied to determine the likelihood of observing the same proportion of 'hotspots' with the sample size

applied in this study. As noted with respect to the previous GM tests, data generated from investigations provided small sample sizes for laboratory analysis and therefore very little evidence to corroborate an AGM was occurring at the location. Sampling patterns generally adhered to the recommended target pattern (Figure 1.2), with only slight deviations from AER recommendations. For the two GM tests considered in this study, spatial sampling was altered to include offset degrees of the cardinal directions (Figure B.3), along with increasing the number of samples for laboratory analysis (Figure 3.1). Expanding the sampling directions was another approach taken to increase the probability of observing a 'hotspot', or location >5 %v/v CH₄, to assess the site for potential risks.

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[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
[REDACTED]	[REDACTED]	[REDACTED]	[REDACTED]
[REDACTED]			
[REDACTED]			

3.5 Conclusions and future work

[REDACTED]

[REDACTED] This study showed how applying a multivariate approach (PCA) can identify environmental interferences and improve sample interpretation. Using six analytically quantified soil gas components (C₁, C₂, C₃, CO₂, O₂, and N₂) and three stable isotopes ($\delta^{13}\text{C-CH}_4$, $\delta^{13}\text{C-CO}_2$, and $\delta^2\text{H-CH}_4$) enabled accurate identification of atmospheric contamination in samples at an abandoned well. A knowledge gap noted in GM tests reported in this study is related to prescreening of soil gases prior to sample collection for laboratory analysis.

[REDACTED]

[REDACTED] Expanding or increasing spatial randomness around the well centre could increase the likelihood of detecting soil gas compositions and stable isotopes that are characteristic of the production zone.³³

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[REDACTED] Fisher's test results based on isotope data indicate higher ratios of hotspots with increasing sample size (Table 3.8) and support the conclusion that isotope data present the best probability for detecting a GM issue at an abandoned well site.

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[REDACTED]

[REDACTED] Additionally, PCA models with sparse distributions could be mitigated with more randomized procedures to ensure sampling sizes that accurately describe the geochemistry of a site. Increasing the spatial distribution of point locations could open up risk assessment methods in GM testing to spatial statistical tools for clustering analysis of sample locations (Getis-ord* hotspot analysis), which are based on geographical information systems (GIS) practices.^{4,6} Using geoprocessing tools in GIS software such as ArcGIS can assist in detecting and analyzing preferential GM pathways from persistent infrastructure failures, locating hotspots, or highlighting problem areas at an abandoned well site.^{6,7}

Additionally, using GIS technology that can generate GPS locations of sampling points with highly accurate spatial coordinates (± 1 cm) would not only aid researchers when accessing open databases but also improve industry monitoring. With more accurate technology, locations from site assessments or GM tests can generate an archive for an abandoned well site for industry operators or consulting companies to access when infrastructure issues persist.

Regardless of spatial accuracy, a standardized sampling approach that can be adjusted radially, as seen in previous investigations and in this study (Figure B.3), will be most effective when GM testing is limited by precautionary measures.

4.1.2 Soil gas sampling protocol

Considerable care was taken to limit atmospheric contamination, as invasive sampling was shown to be the technique least impacted by environmental interactions. Results from this thesis work confirm hypothesis statement and support AER recommendations with respect to using invasive tools for GM testing.¹ Results reported in the first study showed how geochemical characterization of site gases should primarily implement soil probes; if domes are utilized, a verification tool should be paired with these measurements to ensure the accuracy of risk assessments.

A limitation in the sampling protocol of previous investigations (Table 3.1) was the downsizing of samples when submitted to commercial laboratories for characterization. [REDACTED]

[REDACTED] The main issue in previous tests was the lack of correlation between samples characterized in the field and the samples collected for laboratory analysis by service companies. [REDACTED]

[REDACTED]

[REDACTED] Using the techniques reported herein will reduce the number of false negatives or false positives. Results from this thesis indicate standardizing site sampling procedures and streamlining sample assessments in the field with laboratory services is the best practice.

4.1.3 Portable handheld multi-gas monitor

[REDACTED]

[REDACTED] Elevated levels of gases

not only impose an explosive hazard when an ignition source is nearby, but also create an environment where workers maintaining the area could potentially suffocate due to low O₂ levels.⁸ Thesis results support the application of the portable monitor as a worker safety risk assessment tool but not as a definitive monitor for GM testing and supports the initial hypothesis statement for this GM testing recommendation. Study results show the monitor is non-specific with respect to detecting CH₄, has limited accuracy when working above the LEL of CH₄, and is not reliable at measuring CH₄ when the oxygen content is less than 16 %v/v.⁸⁻¹⁰ From detector cross-analysis our results support the use of more analytical detectors, like GC-FID/TCD, to quantify subsurface gas samples (soil gases). When extending the application of this tool to sour natural gas wells—locations where H₂S is present in the production zone—concentrations of sulfur can foul the sensor and incapacitate the monitor.^{8,9}

4.2 Future work

This thesis provides a brief and generalized overview of industry practices for

[REDACTED]

[REDACTED]

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Working towards standardized practices across the natural gas wells can assist Canada in reducing one of the notorious GHG sources in this sector and more specifically aid Alberta in reducing its CH₄ emissions by the year 2025.

4.3 References

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APPENDICES

APPENDIX A Domes and probes



Figure A.1. Dome valve closed (left) and open (right).

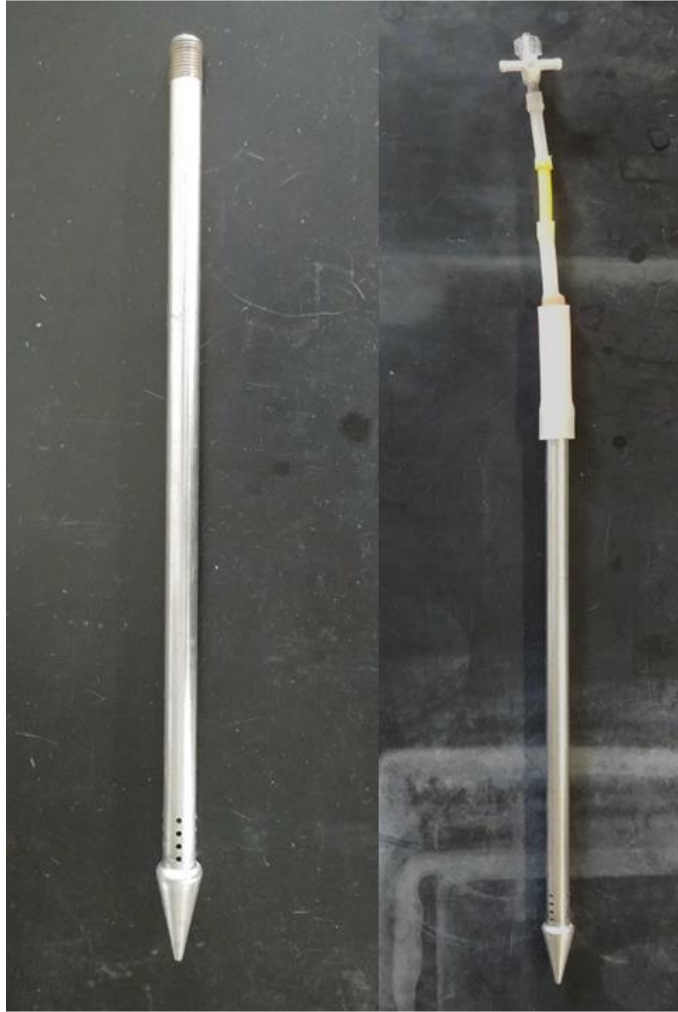
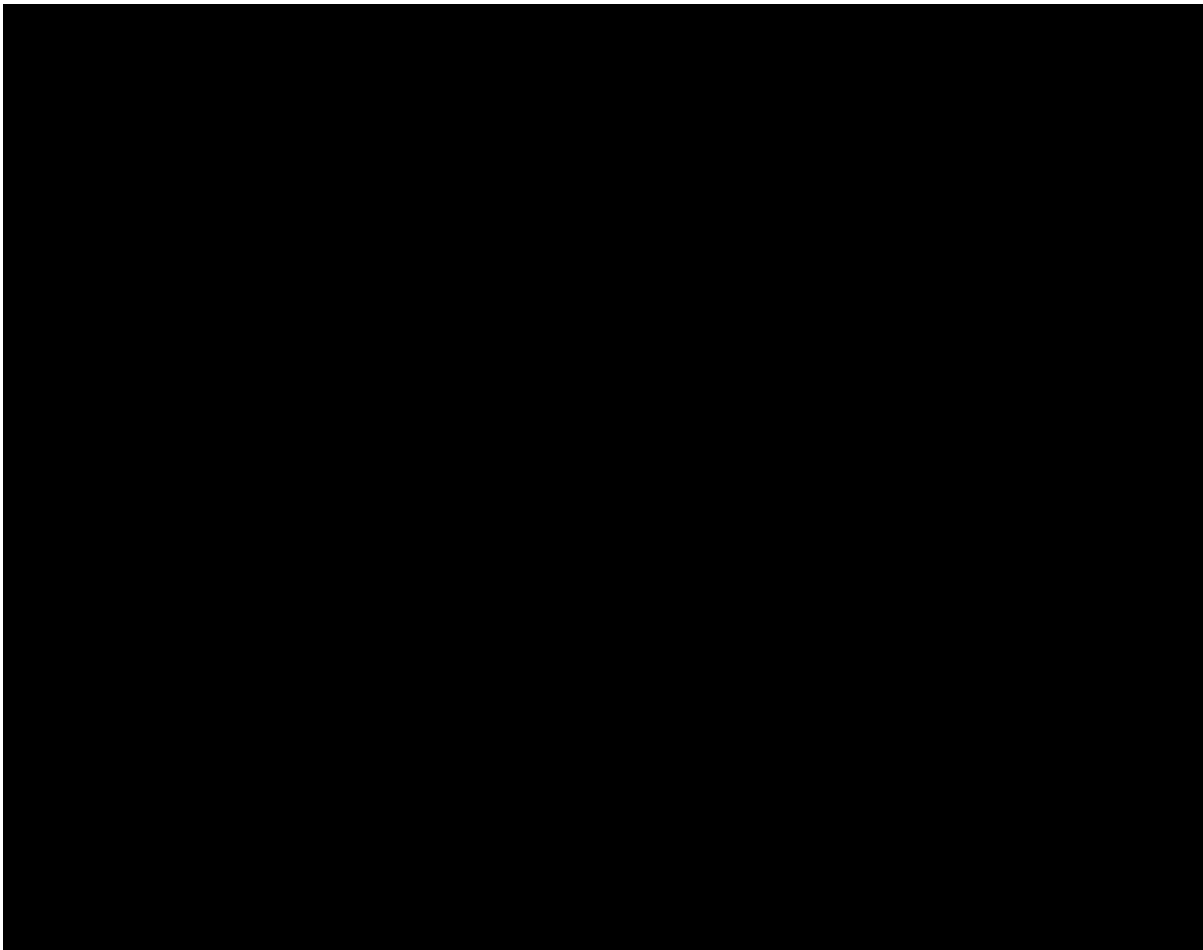


Figure A.2. Probe (left) and probe with sealed tubing and valve (right).



APPENDIX C Non-normalized and normalized field measurements

Table C.1. Agilent 49 micro GC non-normalized and normalized soil gas composition error.

Data Treatment	Non-normalized	Normalized	Non-normalized	Normalized
	<i>Difference (% v/v)</i>		<i>Percent Error (%)</i>	
Total	38.2	59.1	359.4	439.4
Average	1.6	2.5	18.0	22.0

Difference and percent error calculated as absolute value between laboratory and field measurements. Total represents the sum of individual difference and percent error of sample concentrations, while average calculates mean over all sample concentrations.

APPENDIX D Handheld portable multi-gas monitor

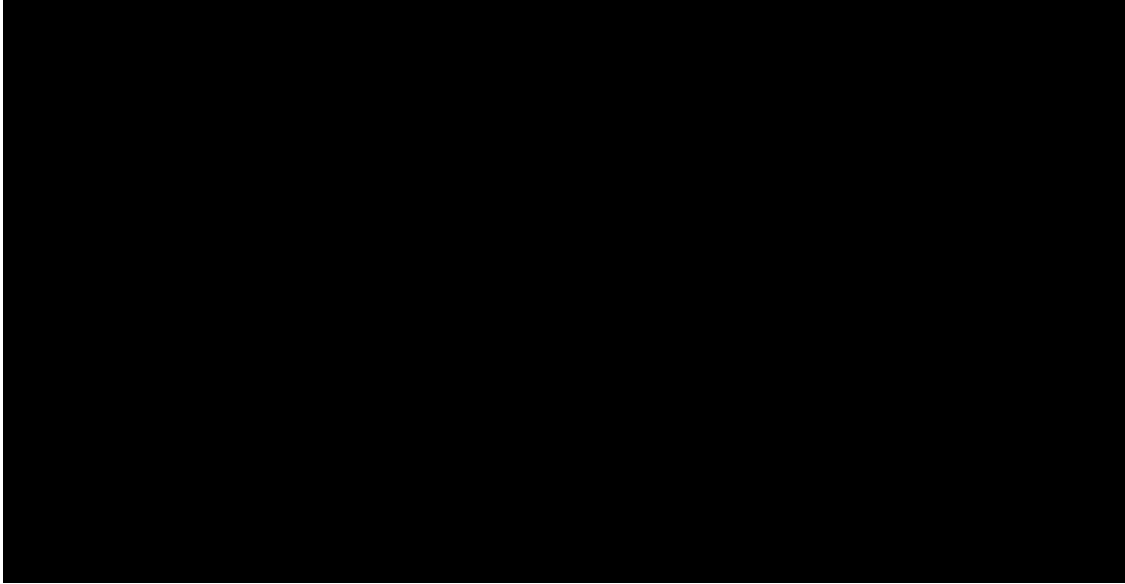


Figure D.4. Component breakdown of portable multi-gas monitor.

APPENDIX E Principal component analysis output

Table E.2. Principal component eigenvalues and variance proportions of soil gas components from 2014 GM investigation.

	PC1	PC2	PC3	PC4	PC5	PC6
Standard deviation¹	2.21	0.888	0.497	0.256	0.122	0.00365
Proportion of Variance	0.814	0.131	0.0411	0.0110	0.00243	0.00
Cumulative Proportion	0.814	0.946	0.987	0.998	1.00	1.00

Standard deviation represents the square root of the eigenvalues of the covariance matrix.¹

Table E.3. PC1 loadings scores of gas components in 2014 GM investigation.

CH ₄	C ₂ H ₆	N ₂	C ₃ H ₈	O ₂	CO ₂
-0.440	-0.435	0.405	-0.401	0.384	-0.379

Table E.4. PC2 loadings scores of gas components in 2014 GM investigation.

CO ₂	O ₂	N ₂	C ₂ H ₆	CH ₄	C ₃ H ₈
0.578	-0.570	0.471	-0.246	-0.206	-0.124

Table E.5. Principal component eigenvalues and variance proportions of soil gas components from 2019 GM investigation.

	PC1	PC2	PC3	PC4	PC5	PC6
Standard deviation¹	2.23	0.783	0.598	0.124	0.0444	0.000215
Proportion of Variance	0.835	0.102	0.0597	0.00259	0.00033	0.000
Cumulative Proportion	0.835	0.937	0.997	0.999	1.00	1.00

Standard deviation represents the square root of the eigenvalues of the covariance matrix.¹

Table E.6. PC2 Loadings scores of gas components in 2019 GM investigation.

C₂H₆	O₂	CH₄	N₂	CO₂	C₃H₈
-0.439	0.431	-0.426	0.422	-0.398	-0.320

Table E.7. PC2 Loadings scores of gas components in 2019 GM investigation.

C₃H₈	N₂	CH₄	O₂	CO₂	C₂H₆
-0.868	-0.336	0.328	-0.112	-0.111	-0.018

Table E.8. Principal component eigenvalues and variance proportions of soil gas components from 2014 and 2019 GM investigation.

	PC1	PC2	PC3	PC4	PC5	PC6
Standard deviation¹	2.02	1.17	0.687	0.244	0.141	0.00273
Proportion of Variance	0.680	0.228	0.0788	0.00991	0.00333	0.000
Cumulative Proportion	0.680	0.908	0.987	0.997	1.00	1.00

Standard deviation represents the square root of the eigenvalues of the covariance matrix.¹

Table E.9. PC1 Loadings scores of gas components in 2014 and 2019 GM investigation.

C₂H₆	CH₄	N₂	O₂	C₃H₈	CO₂
-0.483	-0.470	0.444	0.368	-0.348	-0.303

Table E.10. PC2 Loadings scores of gas components in 2014 and 2019 GM investigation.

CO₂	O₂	C₃H₈	N₂	CH₄	C₂H₆
0.660	-0.554	-0.332	0.310	-0.182	-0.136

Table E.11. Principal component eigenvalues and variance proportions of stable isotopes from 2014 GM investigation.

	PC1	PC2	PC3
Standard deviation¹	1.443	0.907	0.308
Proportion of Variance	0.694	0.274	0.0317
Cumulative Proportion	0.694	0.968	1.000

Standard deviation represents the square root of the eigenvalues of the covariance matrix.¹

Table E.12. PC1 Loadings scores of stable isotopes in 2014 GM investigation.

$\delta^{13}\text{C-CH}_4$	$\delta^2\text{H-CH}_4$	$\delta^{13}\text{C-CO}_2$
0.669	0.622	-0.406

Table E.13. PC2 Loadings scores of stable isotopes in 2014 GM investigation.

$\delta^{13}\text{C-CO}_2$	$\delta^2\text{H-CH}_4$	$\delta^{13}\text{C-CH}_4$
-0.891	-0.433	-0.138

Table E.14. Principal component eigenvalues and variance proportions of stable isotopes from 2019 GM investigation.

	PC1	PC2	PC3
Standard deviation¹	1.41	0.978	0.259
Proportion of Variance	0.659	0.317	0.0233
Cumulative Proportion	0.659	0.977	1.00

Standard deviation represents the square root of the eigenvalues of the covariance matrix.¹

Table E.15. PC1 Loadings scores of stable isotopes in 2019 GM investigation.

$\delta^{13}\text{C-CH}_4$	$\delta^2\text{H-CH}_4$	$\delta^{13}\text{C-CO}_2$
0.698	0.658	0.283

Table E.16. PC1 Loadings scores of stable isotopes in 2019 GM investigation.

$\delta^{13}\text{C-CO}_2$	$\delta^2\text{H-CH}_4$	$\delta^{13}\text{C-CH}_4$
0.938	-0.346	-0.0542

Table E.17. Principal component eigenvalues and variance proportions of stable isotopes from 2014 and 2019 GM investigation.

	PC1	PC2	PC3
Standard deviation¹	1.39	0.964	0.368
Proportion of Variance	0.645	0.310	0.0450
Cumulative Proportion	0.645	0.955	1.00

Standard deviation represents the square root of the eigenvalues of the covariance matrix.¹

Table E.18. PC1 Loadings scores of stable isotopes in 2014 and 2019 GM investigation.

$\delta^{13}\text{C-CH}_4$	$\delta^2\text{H-CH}_4$	$\delta^{13}\text{C-CO}_2$
-0.687	-0.672	-0.276

Table E.19. PC1 Loadings scores of stable isotopes in 2014 and 2019 GM investigation.

$\delta^{13}\text{C-CO}_2$	$\delta^2\text{H-CH}_4$	$\delta^{13}\text{C-CH}_4$
-0.957	0.256	0.134

APPENDIX F

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