# CHARACTERIZATION OF GAS MIGRATION AND SURFACE EMISSIONS THROUGH A CONTROLLED RELEASE EXPERIMENT AT THE HUDSON'S HOPE FIELD RESEARCH STATION, BC, CANADA.

by

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#### Abstract

The expansion of unconventional oil and gas development has led to growing concern regarding the environmental impacts of gas migration (GM), which occurs at some wells. GM is the transport of natural gas outside of the well casing, which can lead to mobile fugitive gas (FG) that penetrates into neighbouring geological formations and can impact aquifers. FG that migrates to the surface contributes to greenhouse gas emissions that are difficult to quantify. This study is part of a research program that aims to increase knowledge of GM and FG through a controlled natural gas release experiment. The experiment was conducted near Hudson's Hope in north-eastern British Columbia, Canada, a region of active unconventional natural gas development. The experimental site is underlain by heterogeneous quaternary deposits with a confining clay layer overlaying a sand aquifer. 100 m<sup>3</sup> of a synthetic natural gas mixture was injected at the base of the aquifer at a constant rate for 66 days.

This thesis focuses on monitoring of GM in the unsaturated zone and the quantification of surface effluxes. To this end, twelve long-term chambers were used to measure  $CO_2$  and  $CH_4$  effluxes, providing high resolution time-series data. Survey chamber measurements at 105 locations allowed for spatially distributed measurements at lower frequency. In addition, soil gas samples were collected from 22 soil gas sampling ports. The results illustrate that the injected gas migrated upgradient against the direction of groundwater flow and broke through at the surface six weeks after the injection started. Once the gas was detected, elevated  $CH_4$  fluxes were continuously detected at the surface in a constrained geographical region and only began to decrease one-week post-injection. Soil gas composition and isotopic data further support that the gas migrated through the soil towards the ground surface and that hydrocarbons were microbially oxidized. The free iii

phase gas plume was only able to reach the surface due to the presence of a preferential pathway in the confining layer. Soil gas compositional data indicates that towards the end of the injection and post-injection, the free-phase gas plume began to explore alternative preferential pathways.

# Lay Summary

In the past decade there has been a rapid expansion of unconventional oil and gas development in North America. Some of these wells have experienced leaks, which are difficult to detect. The presence of leaks can lead to gas migration (GM) away from the primary well. GM is currently not well understood but has the potential to impact aquifers and contribute to greenhouse gas emissions if the gas reaches the surface. This thesis aims to increase knowledge of GM through surface and subsurface monitoring techniques at a controlled natural gas release experiment. The experiment was conducted near Hudson's Hope in north-eastern British Columbia, Canada, a region of active unconventional natural gas development. The results from this thesis are able to provide insights into the fate and transport of GM in the subsurface.

# Preface

This thesis is original, unpublished work and is a part of the University of British Columbia (UBC) Energy and Environment Research Initiative (EERI). The initial Hudson's Hope Field Research Station project design and objectives were produced by Dr. Roger Beckie and Dr. Aaron Cahill. The work done as a part of this thesis was designed by the author and Dr. K Ulrich Mayer. All field data and samples were collected by the author. All chapters were written by the author and edited by Dr. K Ulrich Mayer.

Compositional and isotopic analysis of free phase gas samples were performed at the University of Calgary Isotope Science Laboratory. Data informing the geological cross sections were produced by PhD student Jessie Chao (University of British Columbia). Geophysical data referred to in this thesis is based on work done by a former MSc student, Tim Cary (University of Calgary). Eddy covariance data was collected and processed by current MSc student Chitra Chopra (University of British Columbia).

This research was presented in the form of a talk at the September 2019 Geological Society of America (GSA) conference in Phoenix, Arizona.

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# **List of Abbreviations**

BC: British Columbia

- BCOGC: British Columbia Oil and Gas Commission
- BDL: Below Detection Limit
- bgs: below ground surface
- C<sub>2</sub>: Ethane
- C<sub>3</sub>: Propane
- CFB: Canadian Forces Base
- CH<sub>4</sub>: Methane
- EC: Eddy covariance
- ERT: Electrical resistivity tomography
- FG: Fugitive gas
- GC: Gas chromatograph
- GHG: Greenhouse gas
- GM: Gas migration
- HHFRS: Hudson's Hope Field Research Station
- ISL: Isotope Science Laboratory
- LDAR: Leak detection and repair
- MW2: Monitoring Well 2
- NDFE: Nonlinear diffusive flux estimator
- NGL: Natural gas liquids (defined as ethane, propane, butane, pentane, and heavier hydrocarbons that are produced in the gas stream out of a well)

P/N: Product number
ppb: Parts per billion
ppm: Parts per million
ppmv: Parts per million by volume
STP: Standard temperature and pressure
UBC: University of British Columbia
WCSB: Western Canada Sedimentary Basin

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# Dedication

To my parents, Rossella and David, thank you for your unconditional love and support. Vi voglio molto bene. Questa tesi e per voi.

### **Chapter 1: Introduction**

#### 1.1 Background

Methane (CH<sub>4</sub>) is an efficient greenhouse gas with a warming potential 28 times greater than carbon dioxide (CO<sub>2</sub>) (Intergovernmental Panel on Climate Change, 2014). CH<sub>4</sub> is the most abundant hydrocarbon present in the atmosphere with a lifetime of  $\approx 10$  years (Cicerone & Oremland, 1988; Intergovernmental Panel on Climate Change, 2014). Despite the fact that multiple studies have demonstrated that atmospheric concentrations of CH<sub>4</sub> are rising annually, there is minimal consensus in the scientific community on the controlling mechanisms (Baillie et al., 2019; Bousquet et al., 2006; Fuchs et al., 2016; Kirschke et al., 2013; Lelieveld et al., 1998). The review article by Kirschke et al. (2013) provides an estimate of CH<sub>4</sub> emissions from various CH<sub>4</sub> sources: natural wetlands account for  $\approx 30\%$ , other natural sources (fresh water, wild animals, wildfires, termites, geological, hydrates, permafrost) account for  $\approx 7$  - 19%, incomplete biomass combustion accounts for  $\approx$  5%, agriculture and waste (including landfills) account for  $\approx$  29 - 37%, and fossil fuels account for  $\approx 14$  - 17%. The variability in percent contribution is due to the fact that CH<sub>4</sub> sources and sinks are challenging to quantify and are sensitive to climate and chemical feedbacks, making it difficult to identify specific dominant mechanisms contributing to increased atmospheric CH<sub>4</sub>.

Over the past decade there has been rapid unconventional oil and gas development of tight rock formations in North America, leading to increased natural gas production (Brantley et al., 2014; Cahill et al., 2017; Rogner, 1997; Schneising et al., 2014). Horizontal drilling practices in combination with improved hydraulic fracturing techniques have made resource recovery from low porosity formations technically and economically feasible (Estrada & Bhamidimarri, 2016; Soeder, 2018a). The unintentional release of thermogenic CH<sub>4</sub> (the major component of natural gas) and higher chain n-alkanes from leaking oil and gas wells has been well documented and remains a problem for active, abandoned (not in production) and orphaned (abandoned without ownership) wells (Bachu, 2017; Boothroyd et al., 2016; Cahill et al., 2019; Davies et al., 2014; Ingraffea et al., 2014). This expansion of unconventional oil and gas development in relatively populated regions of North America has contributed to the public concern of the associated environmental hazards; potential groundwater contamination, potential explosion risk, potential vapour intrusion, increased seismic activity and increased unintentional hydrocarbon emissions to the atmosphere (Barth-Naftilan et al., 2018; Caulton et al., 2014; Davies et al., 2014; Jackson et al., 2013; Llewellyn et al., 2015; Soeder, 2018b; Zhang & Yang, 2015). Several public cases, both historical and current, of groundwater contamination and the unintentional release of greenhouse gases (GHGs) from leaking wellbores continue to be an area of concern for the oil and gas industry (Bachu, 2017; Baillie et al., 2019; Chafin, 1994; Jackson et al., 2013; Saponja, 1999; Soeder, 2012, 2018a; Vengosh et al., 2014). For the purpose of this thesis, leaking wellbore refers to a wellbore that is structurally compromised in either its cementation and or casing, causing a loss of zonal isolation and providing potential pathways for a fluid (from either the production zone and or intermediate zones) to move into neighbouring formations. The unintentional release of a gas outside of primary well casings is referred to as gas migration (GM). Once the gas migrates into the neighbouring geological formation it is referred to as fugitive gas (FG) (Cahill et al., 2019; Fox et al., 2019). Figure 1.1 illustrates a basic conceptual model of potential GM and FG migration pathways associated with oil and gas wells (Cahill et al., 2019). Based on Figure 1.1, once the thermogenic CH<sub>4</sub> is mobile, it is able to migrate as a free phase fluid (laterally and vertically via buoyancy driven forces), dissolve in the groundwater, undergo oxidation to produce  $CO_2$  (and other potential bi-products), and diffuse into the atmosphere contributing to GHG emissions.



**Figure 1.1:** Conceptual model of gas migration and fugitive gas migration pathways. Adapted from Cahill et al. (2019).

The majority of fugitive emissions from leaking oil and gas wells are reported to have resulted from wellbore-integrity failure (Cahill et al., 2019; Forde, et al., 2019; Vengosh et al., 2014). There are a wide range of reported confounding factors that can result in the loss of wellbore integrity (Boothroyd et al., 2016; Davies et al., 2014). These factors can be influenced by drilling methods, well age, type of well, casing material, geology, cementation methods and materials. The most common causes of wellbore-integrity failure are associated with improper cement seals and corrosion of the casing (Boothroyd et al., 2016; Jackson, 2014; Ziemkiewicz et al., 2014). Reported literature rates of wellbore-integrity failure and gas migration vary depending on the statistical methodology and dataset selection. Davie et al. (2014) drew on a variety of datasets to determine

wellbore-integrity failure rates worldwide. They reported that in Pennsylvania, US, 6.3% of the 8030 unconventional wells spudded between 2005 and 2013 had well-integrity failures. A study by Vidic et al. (2013) done using a similar dataset for Pennsylvania wellbores determined that 3.4% of 6466 active wells spudded between 2008 and March 2013, had wellbore-integrity failures, less than that concluded by Davie et al. (2014). However, another study by Ingraffea et al. (2014) done in the same study area with a similar dataset concluded that between 2000 to 2012 wellboreintegrity failure was 0.7 - 9.1% of the 32,678 active oil and gas wells. Although the reported wellintegrity failure percentages are relatively similar there is still a significant range in reported values. In the Santa Fe Springs Oilfield in California a wellbore failure rate of  $\approx 75\%$  was calculated based on the 50 investigated wellbores (Davies et al., 2014). In the United Kingdom a study by Boothroyd et al. (2016), determined that  $\approx 30\%$  of 102 decommissioned onshore wells had soil CH<sub>4</sub> levels which were believed to be indicative of wellbore-integrity failure. Focusing more specifically on Western Canada: out of Alberta's 316,439 spudded wells from 1910 to 2004, 4.6% were reported to have well-integrity failures (Davies et al. 2014). This is a similar result to that reported by Bachu et al. (2017) where 6.6 % of 446,289 wells drilled until 2013 in Alberta were reported to have well-integrity failures. In British Columbia (BC), as of January 2018, GM has been identified in 0.6% of  $\approx$  25,000 oil and gas wells (Sandl et al., 2020). In BC, unconventional gas production increased from 20% to 60% of B.C.'s total gas production from 2005 to 2012 and it is expected to continue to increase annually (Rivard et al., 2014). Many of the papers mentioned above undertook a statistical analysis to assess factors that contribute to wellbore-integrity failure. However, currently it has not been possible to identify a specific attribute that is associated with greater risk of wellbore-integrity failure (Sandl et al., 2020). A range of interdependent factors that were closely tied to the local geology were seen to contribute

to instances of GM and therefore, at present, it is not possible to identify controlling mechanism for subsurface GM with confidence.

Despite previous studies investigating GM and wellbore-integrity failure the frequency and controlling mechanisms surrounding GM and fugitive emissions are still not well understood (Brandt et al., 2014; Brantley et al., 2014; Cahill et al., 2019; Cathles et al., 2012; Kemp et al., 2016; Kirschke et al., 2013; Schneising et al., 2014; Schwietzke et al., 2016). Fugitive emissions are difficult to quantify because of uncertainties associated with determining: 1) where the natural gas originates from, 2) where the leak is occurring, 3) magnitude of leakage rates, 4) duration of the leak, and 5) the distribution of FG migration pathways (Cahill et al., 2019; Vengosh et al., 2014). Various technologies have been deployed by operators and regulatory agencies as part of leak detection and repair (LDAR) campaigns (Fox et al., 2019). These technologies range from hand-held monitoring devices to complex multicomponent monitoring systems to quantify and manage fugitive emissions (Fox et al., 2019). At present these methods are only applied if there is a suspected leak near the well head. Therefore, to accurately understand the environmental impact of unconventional oil and gas development for policymakers, investors, and other stakeholders, a better understanding of fugitive gas on both a local and regional scale is required. This thesis focuses on evaluating the transfer of fugitive gas across the water table, assessing its fate in the vadose zone, and quantifying emissions into the atmosphere via a controlled natural gas release experiment.

It is currently known that FG migrates upwards due to buoyancy forces and spreads laterally with the potential to impact aquifers and soils, as well as contribute to greenhouse gas emissions (Cahill et al., 2019; Forde et al., 2019; Vengosh et al., 2014). However, due to a lack of sufficient background sampling, and lack of detailed knowledge surrounding mechanisms of

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fugitive emissions it is not possible to identify the source of contamination with certainty. Controlled gas-release experiments have been conducted to investigate GM associated with subsurface CO<sub>2</sub> leakages, and to investigate fugitive CH<sub>4</sub> migration pathways and rates at landfills (Borjesson et al., 2009; Cahill et al., 2014; Kilgallon et al., 2018; Mønster et al., 2014; Scheutz et al., 2014; Spangler et al., 2010). However, due to numerous unknown variables associated with investigating FG migration at active oil and gas sites, characterization of GM has been limited. Prior to the work performed as part of this thesis, only two controlled release experiments have been conducted in order to gain a deeper understanding of mechanisms controlling GM in the context of oil and gas development. These controlled release experiments proved useful to study GM, because the systems under investigation were substantially better constrained than at operating or abandoned wells. This is because: 1) injected gas volume was known, 2) the gas release point was known 3) appropriate permanent monitoring networks were installed prior to release, and 4) background measurements were conducted. The first controlled release experiment was conducted at the Canadian Forces Base (CFB) Borden, in southern Ontario, Canada. At this site  $\approx 51 \text{ m}^3$  of CH<sub>4</sub> was injected into an unconfined sand aquifer at 4.5 and 9.0 m below ground surface (bgs) over 72 days with dissolved gases monitored for more than 700 days (Cahill et al., 2017; Forde, et al., 2019). The second experiment was conducted in north-eastern BC, above the Montney resource play (Forde et al., 2019). Approximately 30 m<sup>3</sup> of CH<sub>4</sub> was injected 12 m bgs (deeper than the experiment at Borden) into an unsaturated distal glacio-lacustrine deposit for a period of five days (Forde, et al., 2019).

CFB Borden was the first controlled release study that provided detailed subsurface and surface characterization of GM. The site is a relatively homogenous sandy unconfined aquifer, which is not representative of the typical confined aquifers located in the till and fine-grained glaciolacustrine deposits of the Western Canada sedimentary basin (WCSB), where the majority of Canadian oil and gas plays are located (Atkinson et al., 2016). Despite the relatively homogenous lithology at CFB Borden, the experiment was the first to demonstrate that small-scale permeability variations due to varied grain size distribution can impact the movement and extent of GM (Klazinga et al., 2019). Field observations and modelling analysis illustrated that the natural gas was initially driven by buoyancy forces, but then began to spread laterally when encountering lower permeability regions (Klazinga et al., 2019). CH<sub>4</sub> migrated primarily in a free gas phase, and, due to the lower solubility of CH<sub>4</sub> relative to C<sub>2</sub> and C<sub>3</sub>, there was preferential dissolution of C<sub>2</sub> and C<sub>3</sub> into the groundwater (Forde, et al., 2019). Additionally, the free-phase gas migrated 17 m down gradient from the gas release point. This is more extensive than initially anticipated for a relatively homogenous sand aquifer and is more than can be accounted for via groundwater flow (Steelman et al., 2017). Despite periods of constant injection rates the movement of the gas in the subsurface was not continuous, it was hypothesized that a build-up of gas (and therefore pressure) was required to cause breakthrough of gas through overlying lower permeability regions, resulting in episodical fluxes due to discontinuous migration of the subsurface free phase gas (Cahill, et al., 2018; Steelman et al., 2017; Van De Ven & Mumford, 2020).

The second controlled release experiment was located in the WCSB in north-eastern BC where 99% of BC's past and present oil and gas industry development occurs (Sandl et al., 2020). The site contained a deep vadose zone (> 60 m) and was located in a region of active oil and gas development. The main finding of this study was that the amplitude and length of barometric pressure changes directly influenced the occurrence and magnitude of  $CH_4$  effluxes that were measured at the surface (Forde, et al., 2019). The heterogeneity of subsurface lithology was a main governing factor influencing the vertical and horizonal migration of gas in the subsurface (Forde

et al., 2019). Additionally, the short five-day duration of the active gas injection used in this experiment did not allow for the assessment of long-term subsurface leakage.

#### **1.2 Study Motivation of Current Project**

The migration, evolution, and fate of FG that migrates into aquifers in regions of current oil and gas development with complex subsurface lithologies are not fully understood. Additionally, impacts of a large release volume for prolonged periods of time at deeper depths into an aquifer are unknown. Therefore, another multidisciplinary controlled release experiment was conducted to contribute towards closing some remaining research gaps. This experiment location will henceforth be referred to as the Hudson's Hope Field Research Station (HHFRS). The site contains typical regional quaternary deposits with a surface silty diamict confining layer overlying silt and sand units. The geological setting of the HHFRS is relevant as it sits above the Montney resource play, which is located in the WCSB and spans BC and Alberta. It is currently regarded as Canada's most economic gas play that is expected to undergo active exploration for the foreseeable future.

Roughly 100 m<sup>3</sup> of a synthetic natural gas mixture was injected at a constant rate of  $\approx 1.50$  m<sup>3</sup>d<sup>-1</sup>, 26 m bgs at the base of a confined saturated layer, for a period of 66 days in the summer of 2018. A comprehensive monitoring network comprised of three electrical resistivity tomography (ERT) lines, 22 multilevel groundwater wells, 5 single screen pumping wells, an eddy covariance (EC) tower, a weather station, 22 soil gas wells, and 12 dynamic long-term chambers was permanently installed at the site. In addition, the spatial distribution of gas effluxes was characterized using survey chamber measurements.

This thesis focuses on characterizing gas effluxes across the land-surface-atmosphere boundary, and gas composition in the adjacent near-surface soil using a gas-flux chamber method and gas-sampling wells. Automated non-steady state closed dynamic chambers were used to determine CH<sub>4</sub> and CO<sub>2</sub> effluxes over a particular region of the soil by analyzing the rates of concentration change over a measurement period in the chamber headspace (Kutzbach et al., 2007; Pirk et al., 2016). Soil gas wells were used to collect soil gas samples at two depth-discrete intervals to determine the concentration and isotopic signature of the gases present in the soil to help infer subsurface GM pathways and processes.

The ERT surveys detect changes in electrical properties of the bulk subsurface and are able to indirectly detect the increase in saturation of an immiscible gas, which has a significantly higher electrical resistance relative to water-saturated porous media. The ERT surveys and interpretation were conducted by Tim Cary (University of Calgary). The multilevel and single screen groundwater wells were used to collect water samples to assess the geochemical impact and migration of the fugitive gas in the subsurface. The groundwater sampling and analysis was conducted by Jessie Chao (University of British Columbia (UBC)). The EC system was comprised of raised open CH<sub>4</sub>, and CO<sub>2</sub> analysers that measure gas exchanges and effluxes across a large area. The on-site weather station measured: wind speed, wind direction, temperature, barometric pressure, humidity, precipitation, soil moisture. The EC and weather station data processing and take down was done by Chitra Chopra (UBC).
# **1.3** Thesis Objectives

The overarching objective of this thesis is to better understand the fate and transport mechanisms of fugitive CH<sub>4</sub> in the vadose zone and near surface, at the HHFRS controlled release experiment, a site that is representative of north-east BC.

Specifically, within this topic, this thesis aims to:

- I. Characterize the temporal evolution of surface CH<sub>4</sub> and CO<sub>2</sub> effluxes.
- II. Characterize spatial distribution of CH<sub>4</sub> and CO<sub>2</sub> effluxes.
- III. Estimate volume of CH<sub>4</sub> released to the atmosphere.
- IV. Evaluate the influence and correlation of CH<sub>4</sub> and CO<sub>2</sub> effluxes with barometric pressure, wind speed, temperature, precipitation.
- V. Evaluate the relationship between chamber efflux data and EC efflux data.
- VI. Characterize CH<sub>4</sub> and CO<sub>2</sub> concentrations, concentration gradients and fluxes in the vadose zone. To assess the distribution and migration of the free phase gas plume.
- VII. Use stable carbon and hydrogen isotopes to assess CH<sub>4</sub> oxidation in the vadose zone.
- VIII. Assess the ability and utility of a portable mass spectrometer (miniRUEDI) to detect trace gases in the field in real time.

#### 1.4 Thesis Layout

This thesis has been formatted into 5 main chapters:

### I. Introduction

The introduction summarizes previous studies on GM and FG migration in the North American context. Since GM is poorly understood the introduction presented literature on current estimates of GM as well as reasons explaining the difficulty associated with studying GM and FG. Literature of past released experiments to investigate GM was and a basic overview of the motivation and outline of the HHFRS project was discussed.

### II. Methodology

This chapter describes the field site (HHFRS) geology, the experimental injection design and details of the techniques used for collecting and analysing soil gas samples and surface efflux. Additionally, the descriptions of monitoring techniques that were used by other students are also introduced.

# III. Surface efflux measurements and results

This chapter presents the  $CH_4$  and  $CO_2$  efflux data collected using the chamber method. It contains results of the long-term and survey chamber effluxes. This is followed by a discussion of the influence of meteorological parameters and time of day influences on  $CH_4$  and  $CO_2$ efflux data. The chamber method  $CH_4$  effluxes are shown side by side with EC  $CH_4$  efflux data to assess whether the temporal responses of effluxes are comparable. Lastly, cumulative  $CH_4$ emissions to the atmosphere are estimated with the chamber efflux data.

# *IV.* Gas composition and isotopic measurements and results

This chapter presents the results and interpretation of the composition and isotopic measurements of soil gas samples collected across the HHFRS. The composition measurements give insights to potential injection GM pathways, while the isotopic measurements provide supporting evidence for the fate of the gas in the vadose zone. Finally, the insights provided by the miniRUEDI mass spectrometer are described.

# V. Conclusion

The conclusion integrates the main findings of Chapter 3 and Chapter 4. The conclusion discusses the implications of these findings in the context of increased oil and gas development in BC as well as providing insight to the limiting factors of this study.

# **Chapter 2: Experimental Methodology**

### 2.1 Introduction

This chapter describes the field site (HHFRS), including a review of the site geology, the experimental injection design and techniques used for collecting and analysing soil gas samples and surface efflux data using the chamber method. The descriptions of monitoring techniques that were used by other students are also introduced, since data collected with the methods is presented in subsequent sections of this thesis.

### 2.2 Description of Field Site Geology

The HHFRS is located in the uplands of the Peace region 15 km north-east of the town of Hudson's Hope in north-east BC, Canada (Hartman & Clague, 2008). The Peace River Valley experienced significant periods of glaciation and retreat: three from the Laurentide and two from the Cordilleran ice sheets (Hartman & Clague, 2008). As a result, the area is generally flat with rolling hills of quaternary deposits and the underlying sediments are a mixture of accumulations of glacial till, glaciolacustrine deposits, organic-rich layers as well fluvial sediments that were deposited during interglacial periods (Hartman & Clague, 2008). Preliminary interpretations by Best et al. (2017) suggest that in the vicinity of the HHFRS, large buried channel structures filled with predominantly coarse sediments were present, which could provide preferential pathways for gas migration. This is further supported by Ramanathan et al. (2010) who found that buried fluvial and glaciofluvial systems result in significant and complex heterogeneities with varying degrees of interconnectivity of highly permeable units. The HHFRS is vitally important for understanding GM because it is located in a region of active oil and gas development where GM could occur.

Electrical resistivity tomography (ERT) lines, cone penetration tests (CPT), air rotary and sonic drilling were used to characterize the subsurface at the HHFRS prior to the gas injection. Three ERT profiles prior to injection provide evidence for significant heterogeneity both laterally and vertically at the field site (Cary, 2019). A total of 27 wells (22 multi-level wells and 5 observation open wells) were drilled to depths greater than 15 m and core logging (Figure 2.1) indicates that the near surface is comprised of a 12 m thick silty diamict till unit with stiff clay, variable grain size including isolated drop stones, up to cobble sized (Chao et al., in preparation). During well installation, no macropore, fractures or preferential flow paths that could serve as conduits for a free-gas phase were observed. The confining diamict is underlain by 10 to 20 m of saturated interstratified coarser-grained fine to medium sand fluvial deposits. The water table is located between 1.5 and 3.0 m below the ground surface. The interpreted groundwater flow direction is from north-west to south-east, based on hydraulic head measurements from five observation wells at the site. The flat topography across the site results in a low groundwater flow gradient and groundwater flow rate (Cary, 2019). The sediments at the HHFRS site are typical of surface sediments found in north-eastern BC and therefore, the site provides an ideal setting to assess the impact of gas migration in an area of significant oil and gas exploration and production (Best et al., 2019; Cary, 2019; Chao et al., in preparation; Hartman & Clague, 2008; Levson, 2008).



**Figure 2.1:** (A): Field site marked by a red star (lat: 56.167871°, lon: -121.850922°) located in north-eastern British Columbia, Canada. Part (A) was adapted from Sandl et al. (2020). (B) Monitoring network at the field site. (C): Core logs collected from CPT drilling at 3 locations as indicated on the field site. (C): Core logs collected from CPT drilling at 3 locations as indicated on the field site. (C): Core logs collected from CPT drilling at 3 locations as indicated on the field site. (C): Core logs collected from CPT drilling at 3 locations as indicated on the field site. (C): Core logs collected from CPT drilling at 3 locations as indicated on the field site. (C): Core logs collected from CPT drilling at 3 locations as indicated on the field site. (C): Core logs collected from CPT drilling at 3 locations as indicated on the field site. (C): Core logs collected from CPT drilling at 3 locations as indicated on the field site. (C): Core logs collected from CPT drilling at 3 locations as indicated on the field site monitoring network, the cores generally illustrate a confining silt diamict layer for the first 12 m with layered medium to fine sand below. Additionally, the angled gas injection well and its relative location is marked on the figure.

### 2.3 Injection Configuration

The injection was configured to release a synthetic natural gas mixture at the base of the aquifer at the HHFRS allowing upward migration of gas through the entire thickness of the aquifer. The single screen injection well was drilled at a 45° angle from the surface to a depth of 26 m bgs (Figure 2.1). It was drilled roughly orthogonal to the groundwater flow direction in a north-east to south-west direction. The synthetic natural gas was composed of 85% methane and 8% ethane, which was synthesized to match the composition of natural gas of the Montney resource play found in the area (Table 2.1) (Cahill et al., 2019). Butane was not included in the synthetic gas mixture due to cost constraints. The remaining 7% of the synthetic injection gas was composed of slightly elevated levels of propane, carbon dioxide, nitrogen, and helium compared to locally produced natural gas (Table 2.1). Helium was included to act as a non-reactive gaseous tracer and carbon dioxide and nitrogen were added to compensate for the lack of butane. This experiment differs from previous controlled injection experiments where pure CH<sub>4</sub> was injected into the subsurface (Cahill et al., 2018b; Forde et al., 2018; Klazinga et al., 2019). The experiment was designed to simulate the impacts of fugitive gas migration in the Montney resource play as closely as possible. A total of  $\approx 100 \text{ m}^3$  of a thermogenic synthetic gas mixture was injected into the subsurface using a mass flow controller to deliver gas at a rate of  $\approx 1.5 \text{ m}^3$  per day for 66 days between June 12 and August 17, 2018.

**Table 2.1:** The composition of the synthetic gas (% v/v) used for the experiment in comparison to typical Montney gas (Cahill et al., 2019). Abbreviations: CH<sub>4</sub>, methane; C<sub>2</sub>, ethane; C<sub>3</sub>, propane; C<sub>4</sub>, butane.

Gas (%v/v)	CH4	<b>C</b> <sub>2</sub>	<b>C</b> <sub>3</sub>	C <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub>	Не
Typical Montney Gas	0.85	0.08	0.03	0.02	0.001	0.002	0.0001
Synthetic Montney Gas	0.85	0.08	0.05	0	0.01	0.005	0.005

### 2.4 Surface CH<sub>4</sub> and CO<sub>2</sub> Efflux Measurements

### 2.4.1 Field Installation of Efflux Chambers

Surface effluxes were measured using long-term (Figure 2.2. (A)) and survey (Figure 2.2 (B)) nonsteady state opaque dynamic closed chambers. Photographs of the field installation of long-term chambers and a survey chamber measurement are provided in Figure 2.2. The dynamic chamber method determines fluxes by analyzing the rates of gas concentration change in a chamber headspace over a measurement period (Kutzbach et al., 2007; Pirk et al., 2016). Long-term chambers are permanently installed and continuously and sequentially collect measurements. Survey measurements are collected by moving the analysers to collar locations (green rings on the ground shown in Figure 2.2) and taking measurements over a large area.



**Figure 2.2:** (A) Photograph of the permanently installed long-term automated chambers that are co-located with the soil gas wells. The long-term chambers are sitting on green collars and have tubing that runs from the automated chamber to the LI8100 (CO<sub>2</sub> and  $H_2O_{vapour}$ ) and the 907-0011 GHG analyser (CO<sub>2</sub>,  $H_2O_{vapour}$  and CH<sub>4</sub>). (B) is a photograph taken of the survey chamber while it is actively taking a measurement. The survey chamber is lifted using the handle at the top and is placed on a collar and then the LI8100 (CO<sub>2</sub> and  $H_2O_{vapour}$ ) and UGGA (CO<sub>2</sub> and  $H_2O_{vapour}$  and CH<sub>4</sub>) analysers in the cart are used to take a measurement. Once a measurement is complete the chamber and analysers are moved to the next measurement location.

To obtain representative flux measurements from the subsurface, all chambers (long-term and survey) were placed on top of a collar with new gaskets to ensure a tight gas seal. For this experiment, green opaque polyvinyl chloride (PVC) collars with a 20 cm internal diameter and a 317.8cm<sup>2</sup> internal surface area were used (see green rings in Figure 2.2). They were installed 10 cm into the ground, leaving an average 4 cm of the collar above the ground. For each collar, the stick-up above ground surface was individually measured at three locations (every 120°) and averaged, to accurately calculate the headspace volumes. The collars were installed at all 117 monitoring locations a minimum of three days prior to the deployment of the chambers. The depth of collar insertion and three-day wait period ensured a good seal between the collar and the surrounding soil, while allowing the soil to recover from disturbances resulting from installation, therefore providing more representative measurement results (Rochette et al., 1997). The site soils were characterized by variable porosity, justifying the insertion depth of 10 cm, which limits lateral diffusion in the subsurface in the measurement region (Brændholt et al., 2017; Davidson et al., 2002; Hutchinson & Livingston, 2001).

The initial experimental set up for time-series measurement of soil gas effluxes consisted of twelve automated long-term dynamic non steady state chambers (LI-8100-104, LI-COR Inc.), deployed in two spokes of six chambers. The first spoke trended roughly north-south and the second spoke trended roughly east-west (Figure 2.3). This design was chosen because the previous CFB Borden experiment suggested that GM in the subsurface was potentially influenced by groundwater flow direction, therefore, one of the spokes was set-up trending in the direction of groundwater flow (Cahill et al., 2018b; Forde et al., 2019). The second spoke was set up perpendicular to the first spoke to capture the distribution of effluxes orthogonal to the groundwater flow direction. Previous controlled release studies demonstrated that FG broke through at the surface in relatively close proximity to the release point (e.g.: Forde et al., 2019) and as a result the survey chamber collar locations (blue dots in Figure 2.3) were arranged in a telescoping fashion with a closer density more proximal to the gas release point.



**Figure 2.3:** An image of the experimental set up and monitoring network for the vadose zone and surface efflux measurements. The blue dots represent locations with survey collars, the yellow triangle represent the initial location of the long-term chambers, the green hexagon represents the gas release points and the crosses represent initial soil gas well locations. The black triangle represents the intermediate long-term chamber location and the orange diamonds represent the new locations of the moved long-term chambers. The red square represents monitoring well 2 (MW2) and the purple triangle represents the eddy covariance system.

#### 2.4.2 Long-term Chamber Measurements

The twelve vented automated long-term dynamic non steady state chambers were connected to a multiplexer (LI-8150, LI-COR Inc.), which fed the gas to an infra-red gas analyser (LI-8100A, LI-COR Inc.) that measured  $H_2O_{vapour}$  and  $CO_2$  concentrations, and an extended-range (0.01—100, 000ppm) greenhouse gas analyser (GGA 907-0011, Los Gatos Research Inc.) that measured

H<sub>2</sub>O<sub>vapour</sub>, CO<sub>2</sub> and CH<sub>4</sub> concentrations. The Licor systems controlled the chamber settings and allowed for time-series measurements at all monitoring locations at a high temporal resolution (a measurement taken every second), with the twelve-chamber measurement cycle taking approximately one hour to complete. A schematic of the long-term chamber set up and operation is depicted in Figure 2.4.



**Figure 2.4:** The long-term chambers were connected to a multiplexer which feeds gas emitted from the subsurface to an infra-red gas analyser (LI-8100A, LI-COR Inc.) and an extended range (0.01—100 000 ppm) greenhouse gas analyser (GGA 907-0011, Los Gatos Research Research Inc.). (A): the long-term chamber is initially open when not taking measurements. (B): when the chamber is set to take a measurement the arm swings and sits above the collar.

(C): after the chamber bowl is physically above the collar, it is lowered and once a seal is created the measurement cycle begins.

The long-term chambers collected measurements at the field site continuously from May 24, until October 2, 2018. The system was taken down on October 2, 2018, as freezing conditions set in. On July 24, 2018, free-phase gas was observed coming out from a groundwater sampling port of monitoring well 2 (MW2), 12 m north-west of the gas release point (Figure 2.3), upgradient topographically and in the opposite direction of groundwater flow. The composition of dissolved gas and free phase gas collected from MW2 was measured in the field by the miniRUEDI portable mass spectrometer (see section 2.5.2). The MiniRUEDI measured dissolved concentrations of He and CH<sub>4</sub> up to 1000 times above atmospheric concentrations, and the free gas composition was very similar to the synthetic injection gas, providing immediate confirmation that the gas observed was the injection gas introduced to the system. To spatially characterize GM and surface emissions around MW2, a 14 m by 12 m survey grid with one meter spacing was established around MW2 (Appendix A). Survey chamber measurements of CO<sub>2</sub> and CH<sub>4</sub> effluxes were taken at each node location of the grid to determine regions of highest efflux. Based on the data collected on July 25, 2018, the long-term chambers placed along the spoke trending generally west to east were relocated to form the north-west spoke in Figure 2.3 (depicted by orange diamonds).

### 2.4.3 Survey Chamber Measurements

Survey efflux measurements were collected with a portable survey chamber (LI-8100-103, LI-COR Inc.) connected to an infrared gas analyser (LI-8100A, LI-COR Inc.) that measured  $H_2O_{vapour}$  and  $CO_2$  concentrations and an ultraportable greenhouse gas analyser (915-0011, Los Gatos Research Inc.) that measured  $H_2O_{vapour}$ ,  $CO_2$  and  $CH_4$  concentrations. A total of 12 rounds of

survey efflux measurements were taken between June 1 and September 28, 2018. For each survey, measurements were collected at up to 105 locations on the monitoring grid shown in Figure 2.3. The portability of survey chambers allowed surveying of fluxes over a large area with relatively fine resolution. A schematic of the survey chamber set-up can be seen in Figure 2.5 and the survey chamber collar locations are shown in Figure 2.3.



**Figure 2.5:** The vented survey chamber fed the gas directly to an infra-red gas analyser (LI-8100A, LI-COR Inc.) and an extended range (0.01—100 000ppm) ultraportable greenhouse gas analyser (GGA 907-0011, Los Gatos Research Inc.). (A): the survey chamber is placed above the desired location using the handle. (B): when the chamber is set to take a measurement, it lowers itself and once a seal is created the measurement cycle begins.

### 2.4.4 Flux Calculations

An exponential function based on a simplified diffusion theory using Fick's first law was used for flux estimates (Brændholt et al., 2017; Davidson et al., 2002; Kutzbach et al., 2007; Venterea, 2010). The closed chamber method leads to an increase in gas concentrations in the chamber headspace, resulting in a change in the concentration gradient between the soil and chamber headspace; leading to a non-linear change in headspace gas concentration as a function of time (Brændholt et al., 2017; Davidson et al., 2002; Hutchinson & Livingston, 2001; Kutzbach et al., 2007; Venterea, 2010). As a result, linear regressions tend to underestimate fluxes, while the exponential approach is appropriate for a larger range of scenarios and result in more representative flux estimations. Livingston et al. (2006) developed a nonlinear flux calculation referred to as the nonlinear diffusive flux estimator (NDFE), which was further refined for easier application by Venterea (2009). However, Kutzbach et al. (2007) compared various models to calculate fluxes and concluded that the difference between NDFE and the exponential model was minimal and therefore the more simplistic exponential model was used for all calculations in this thesis.



**Figure 2.6:** Soil CO<sub>2</sub> flux data collected on June 10, 2018 at HHFRS. The observation length was 150 seconds, dead band of the pre-purge and the first data point used in the analysis is collected after the dead band. Observation:  $t_0 = 20s$ ,  $C_0' = 405$  ppm. The hollow gray circles represent a measurement points taken every second, the blue line illustrates an exponential fit to the raw data and the red line illustrates a linear fit to the raw data.

The flux,  $F_c$ , is then determined by applying an exponential fit to the temporal gradient of the concentration data  $\frac{\partial C}{\partial t} \left( \frac{\partial CO_2}{\partial t} \text{ and } \frac{\partial CH_4}{\partial t} \right)$ . The equation used is:

$$F_{c} = \frac{10VP_{0}\left(1 - \frac{W_{0}}{1000}\right)}{RS(T_{0} + 273.15)} \frac{\partial C}{\partial t}$$
(Equation 2.1)

where  $F_c$  is the gas efflux (µmol m<sup>-2</sup>s<sup>-1</sup>),  $P_0$  is the initial pressure measured inside the chamber (kPa),  $W_0$  is the initial water vapor mole fraction (mmol mol<sup>-1</sup>),  $\frac{\partial C'}{\partial t}$  is the initial rate of change in water-corrected CO<sub>2</sub> and CH<sub>4</sub> mole fraction after the deadband (µmol mol<sup>-1</sup>), S is the soil surface area over which the flux occurs (the inner area of the surface collars, m<sup>2</sup>), *V* is the total volume of the system (the sum of the volume of the chamber headspace, volume of the collar above the ground surface, associated connection tubing, and the internal analyser volume for both the LI8100 and GGA 907-0011), *R* is the ideal gas constant (8.314 Pa m<sup>3</sup> K<sup>-1</sup> mol<sup>-1</sup>), *T*<sub>0</sub> is the initial air temperature (°C) and P<sub>0</sub> is the initial air pressure measured by the analyser (kPa)

To calculate the fluxes using Equation 2.1, the initial concentration gradients  $\frac{dC'}{dt}$  are required for CO<sub>2</sub> or CH<sub>4</sub>. Figure 2.6 illustrates that after the dead band period of a measurement cycle, mixing in the chamber is stable and the observational concentration data can be fit with the following empirical exponential equation (LI-COR Biosciences, 2015; McDermitt et al., 2007; Rochette et al., 1997):

$$C'(t) = C_{x'} + (C_{0'} - C_{x'})e^{-a(t-t_{0})}$$
(Equation 2.2)

where C'(t) is the instantaneous water-corrected trace gas mole fraction in the chamber,  $C_x$  is a parameter that defines the measured µmol of the trace gas per mol dry air (µmol mol<sup>-1</sup>),  $C_0'$  is the value of C'(t) after the dead band and *a* is a parameter that defines the curvature of the fit (s<sup>-1</sup>). The initial gradient  $\frac{dC'}{dt}$  can be derived from this fitted function for use in Equation 2.1.

Chamber measurement parameters were determined based on field testing prior to the official data collection start date. The set-up and measurement approach for long-term and survey chambers generally follows the approach outlined by Sihota et al. (2013) and utilizes the parameters specified in Table 2.2 (Kutzbach et al., 2007; Pirk et al., 2016).

Measurement	Time (Seconds)
Pre-Purge	35
Post-Purge	60
Measurement Period	210
Time Between Subsequent Measurement	5
Dead Band	20

Table 2.2: Setting specifications used for all chamber-based measurements.

Once all individual survey measurements were completed, the spatial effluxes were interpolated with a linear ordinary kriging technique using a built-in function in Python. A total of twelve interpolation techniques were evaluated using a Python script. For each interpolation method the minimum values, maximum values and means were assessed as well as the image of the final output. The linear kriging technique was deemed the most suitable as it is a multi-step interpolation based on spatial statistical relationships between data points. Additionally, kriging has been shown to be a successful interpolation technique in various studies with heterogeneous datasets (Goovaerts, 2008; James & Freeze, 1993; Vargas-Guzmán, 2010). The general form of the formula for the interpolator is the weighted sum of the data:

$$Z(s_0) = \sum_{i=1}^N \lambda_i Z(s_i)$$
 (Equation 2.3)

where,  $Z(s_i)$  is the measured value at the *i*th location,  $\lambda_i$  is an unknown weight for the measured value at the *i*th location,  $s_0$  is the prediction location and N is the number of measured values.

#### 2.5 Gas Chemistry in Unsaturated Zone

### 2.5.1 Soil-Gas Samples

Soil-gas samples for measurement of gas concentration and stable isotopes were collected from 22 soil-gas sampling locations across the site with ports at 0.45 m bgs and 1.15 m bgs resulting in 44 sampling ports (Figure 2.7). An Eijkelkamp Augering kit for heterogeneous soils was used to auger three-inch-diameter soil-gas wells. A sampling tubing was centered in the borehole and layers of alternating sand and bentonite were placed as shown in Figure 2.7. After each layer of dry bentonite pellets was added, water was poured to swell the bentonite and create a seal. The soil-gas tubing consisted of  $\frac{1}{4}$  inch outer diameter polyethylene tubing with a one-inch fine mesh screen (198 x 198 with a 0.0035" opening size. P/N: McMaster Carr 9318T47) at the bottom and a gas-tight ball valve at the top. A total of 14 rounds of samples were collected, 13 of which were collected between June 1, and September 13, 2018, and one on June 25, 2019. A pressure gauge linked to Masterflex tubing attached to a peristatic pump was connected to the ball valve while collecting gas samples. The pressure was monitored while sampling to ensure it remained close to atmospheric, to ensure that air was not entrained, and the collected sample was representative of the soil-gas at the screen depth. Three well volumes were purged using a peristaltic pump and gastight syringe (Valco Instruments CO.). A 20 mL sample of soil-gas was then collected via gastight syringe and then transferred to a pre-evacuated 12 mL vial (Labco Exetainer P/N 837W).



**Figure 2.7:** Soil-gas sampling field set up. The diagram illustrates the two sampling tubes collecting samples from 0.45 and 1.15m bgs that were attached to gas tight ball valves. A pressure gauge and peristatic pump with a gas tight syringe was used to collect gas samples.

Samples were analyzed at the Isotopic Science Laboratory (ISL) at the University of Calgary. The methodology outlined in this section was communicated by Michael Nightingale and Stephen Taylor of the ISL (M. Nightingale, personal communication, June 20, 2019; S. Taylor, personal communication, July 30, 2019). Gas compositional analysis (H<sub>2</sub>, He, N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> and C<sub>1</sub> to C<sub>3</sub> alkanes) was completed by injecting a 5 mL aliquot of the above into a Scion 450/456 gas chromatograph (GC). The GC utilizes four separate analytical columns connected to three thermal conductivity detectors and a flame-ionization detector for gas separation and quantification. The lower detection limit for hydrocarbon gasses is 1 ppm and for non-hydrocarbon gasses is 50 ppm.

Analytical precision and accuracy for gas composition analysis is better than  $\pm 2.5\%$  of the reported concentrations.

Stable-carbon isotope ratios  ${}^{13}C/{}^{12}C$  of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, CO<sub>2</sub> and the  ${}^{2}H/{}^{1}H$  of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> were measured using continuous-flow isotope-ratio mass spectrometry. Portions of the original samples were injected using a gas-tight syringe into a helium carrier stream of a Thermo Trace GC for the  ${}^{13}C/{}^{12}C$  and a Thermo Trace GC Ultra for the  ${}^{2}H/{}^{1}H$  ratios. Using this method, the compounds in the sample are separated on the GC column and are then passed through a high temperature combustion reactor (maintained at 1030 °C and 1420 °C for the  ${}^{13}C/{}^{12}C$  and  ${}^{2}H/{}^{1}H$ ratios respectively). After the hydrocarbon species pass through the combustion reactor for the  ${}^{13}C/{}^{12}C$  they are subsequently converted to CO<sub>2</sub> and for  ${}^{2}H/{}^{1}H$  they are converted to H<sub>2</sub> and separated. The CO<sub>2</sub> and H<sub>2</sub> is then sequentially transported via a Thermo Conflo-IV through a water trap and ultimately to the Thermo Scientific MAT 253 mass spectrometer. The isotope ratio values are then calculated using the internal software (ISODAT 3.54). The final results are expressed as  $\delta$  values using per mil notation relative to the international V-PDB and V-SMOW standards (for  ${}^{13}C$  and  ${}^{2}H$ , respectively) with an associated accuracy of  $\pm$  0.5 for  $\delta^{13}C$  and  $\pm$  2 for  $\delta^{2}H$  and a detection limit of 1000 ppmv for  $\delta^{13}C$ .

### 2.5.2 MiniRUEDI

The miniRUEDI (Brennwald et al., 2016), a portable mass spectrometer system developed at the Swiss Federal Institute for Aquatic Science and Technology, was used at the HHFRS during the injection experiment 1) to provide real-time detection and quantification of the injected gas in the subsurface and 2) to provide measurements of helium concentrations (which cannot be measured

using the University of Calgary's ISL GC). The miniRUEDI has the ability to detect a wide range of gases (including He, Ar, Kr, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub>H<sub>8</sub>) in real time.

Soil-gas samples for analysis with the MiniRUEDI were collected in 12 mL pre-evacuated exetainer vials (Labco). Into each vial, 20 mL of soil-gas was injected. To analyze the vial, a needle connected to the miniRUEDI capillary was inserted into the exetainer. The capillary was allowed to flush with sample for two minutes before the analysis started. In the field, the instrument was calibrated by measuring gas in exetainers containing 20 mL of air or 20 mL of injection gas.

The 12 ml exetainers were selected because the volume of gas available from each soil-gas port was limited. Due to the tights soils, it was not possible to collect more than 100 mL of gas from each soil-gas well at a time. Extracting larger samples led to negative pressures relative to the atmosphere or caused drawing water into the sampling syringe. We observed a steady decrease in the signal for all masses over the course of the measurement cycle with the miniRUEDI, which was caused by a decrease in gas pressure inside the exetainer, as sample was withdrawn through the capillary. To minimize this artifact, we reduced the number of measurement cycles per sample from 10 to 5 to reduce the pressure decrease during the sample analysis. Despite the overall drop in pressure, the ratio of the gases remained relatively constant over the measurement cycle and the analyses in terms of percent composition can be considered reliable.

Standards for the miniRUEDI calibration curves were prepared in 250 mL glass serum bottles (Wheaton) sealed with chlorobutyl rubber stoppers and aluminum crimp seals. Each 250 mL bottle contained 400 mL air, to match the pressure in the exetainer vials collected in the field. (The 12 mL exetainer vials were filled with 20 mL of soil-gas.) One vial containing pure air (5 ppm He) was analyzed. Into other bottles, helium (5.0 purity) was injected using a gas tight syringe (Valco Instruments Co. Inc.) to prepare additional standards of 250, 1000, and 5000 ppm He (containing 0.1, 0.4, and 2.0 mL of helium, respectively).

Figure 2.8 depicts the two calibration curves for standards with helium concentrations from 5 to 5000 ppm and concentrations from 5 to 1000 ppm. The estimated precision and accuracy of the helium analyses is 20% of the measured value, based on propagated uncertainty in the reproducibility of replicate analyses, and the uncertainty in the calibration curve, and uncertainties in the preparation and analysis of samples.



**Figure 2.8:** The calibration curve of the measured helium intensity to the helium concentration. The standards used for this calibration curve had helium concentrations between 0 - 5000 ppm for the blue data points and 0 - 1000ppm for the orange data points.

#### 2.6 Additional Monitoring Network

### 2.6.1 Eddy Covariance (EC)

An EC system was installed at the north-east corner of the HHFRS on May 14, 2018 and was actively collecting data from June 11, until November 4, 2018. The EC system was comprised of a 3-D sonic anemometer (CSAT3B, Campbell Scientific, Inc.), an open path LI-COR, Inc. LI-7700 for CH<sub>4</sub>, an enclosed infrared gas analyser LI-COR, Inc. LI-7200 for CO<sub>2</sub> and water vapour and a comprehensive self-contained climate system. Auxiliary climate sensors were subsequently added, and the entire system was fully operational on June 28, 2018 (Cahill et al., 2018a).

The complete EC and climate system allow for the measurement of spatially integrated continuous high-resolution CH<sub>4</sub> and CO<sub>2</sub> effluxes and net exchanges, for the EC flux footprint area, unlike the chambers that are only able to determine effluxes over small surface areas at the selected measurement locations (Baldocchi, 2003). The footprint model used for the EC analysis describes the spatial extent of the surface area that is contributing to EC efflux measurements (Kljun et al., 2015). The extent of the footprint for the EC flux analysis varies for every time average (30 minutes) based on meteorology (wind speed, wind direction and friction velocity), height of the tower and surface roughness (Kljun et al., 2015; Leclerc & Thurtell, 1990; Leclerc & Foken, 2014). In this thesis, efflux data collected using the EC and chamber method are compared in a qualitative fashion, with a focus on timing of efflux events.

### 2.6.2 Electrical Resistivity Tomography Surveys

ERT surveys are a non-invasive method to assess changes in bulk electrical properties of the subsurface. For this experiment, electrical resistivity methods were used to detect the emplacement

of injected gas in the subsurface, possible due to the significantly different electrical properties of gas and water. ERT profiles along three lines (Figure 2.9) were collected at six times using the ABEM terrameter LS 2 from June 5, to September 9, 2018 (Cary, 2019). To ensure repeatable results the electrodes for the three ERT lines with 81 12-inch electrodes per line were left permanently installed. Line 1 from A-B has a 5 m electrode spacing and line 2 section C-D has a 2.5 m electrode spacing. The greater line spacing in Line 1 provides greater depth profiles, while the shorter electrode spacing of Line 2 allows greater near surface resolution (Cary, 2019). Samouëlian et al., 2005). Line 3 runs from E-F and uses a 2.5 m electrode spacing (Cary, 2019). A gradient and dipole-dipole array were used to image all of the profiles in the experiment (Cary, 2019). The five data profiles collected after the start of the experiment were compared to a background profile to assess for the presence of subsurface gas or any subsurface structural changes.



**Figure 2.9:** Site map showing the three ERT lines AB, CD, EF at the HHFRS. The gas release point is located at the center of line CD (adapted from Cary, 2019).

# **Chapter 3: Surface Efflux Measurements**

# 3.1 Introduction

This chapter presents the  $CH_4$  and  $CO_2$  efflux data collected using the chamber method. It contains results and description of the long-term and survey chamber effluxes. The influence of meteorological parameters on  $CH_4$  and  $CO_2$  efflux data is explored, as well as time of day influences. The chamber method  $CH_4$  effluxes are shown side by side with EC  $CH_4$  efflux data to assess whether the temporal responses of effluxes are comparable. Lastly, cumulative  $CH_4$ emissions to the atmosphere are estimated with the chamber efflux data.

# 3.1.1 Chapter Objectives

- I. Characterize the temporal evolution of the surface CH<sub>4</sub> and CO<sub>2</sub> effluxes at select locations.
- II. Characterize the spatial distribution of CH<sub>4</sub> and CO<sub>2</sub> effluxes at selected times.
- III. Evaluate the correlation of CH<sub>4</sub> and CO<sub>2</sub> effluxes with climate data (barometric pressure, precipitation, temperature, diel variations and wind speed).
- IV. Evaluate the temporal correlation between chamber efflux data and EC efflux data.
- V. Estimate the fraction of injected gas released to the atmosphere based on the chamber data.

3.2 Temporal Evolution in Surface Gas Effluxes Based on Long-term Chamber Measurements

### 3.2.1 CH<sub>4</sub> Effluxes from Long-term Chambers

Gas effluxes were monitored using twelve dynamic long-term chambers for 13 days prior to beginning the injection of the synthetic natural gas into the subsurface on June 12, 2018. The locations of the long-term chambers is illustrated in Figure 3.1. Background CH<sub>4</sub> effluxes indicated that at certain times and locations CH<sub>4</sub> emissions occurred from the soil to the atmosphere at very low rates  $(-1 \times 10^{-5} \text{ to } 2 \times 10^{-3} \text{ } \mu \text{mol m}^{-2} \text{ s}^{-1})$ , but the majority of net movement of CH<sub>4</sub> was from the atmosphere into the soil, (i.e. a negative flux), illustrating that soil at the site naturally acts a net CH<sub>4</sub> sink. Based on the 13 days of measured baseline CH<sub>4</sub> effluxes, no consistent pattern in the spatial distribution of CH<sub>4</sub> fluxes was discerned.

CH<sub>4</sub> effluxes greater than 0.01  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>, were first detected during a spatial survey roughly six weeks after the start of the injection (July 25), 12 m upgradient of the gas release point. There were no long-term chambers originally placed in this area. On July 26, one of the long-term chamber measurement spokes (comprised of six chambers) was relocated to align with the region of elevated effluxes (see Chapter 2 and Figure 3.1 Locations LT13 – LT18). One chamber (Location LT13, located 1 m north-west of the gas release point) was moved again on August 7, to a location 15.6 m north-west (LT19), since survey measurements indicated that increased CH<sub>4</sub> effluxes were detected at the new location, while significant effluxes (> 0.01  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) were not measured at the previous location. Therefore, continuous CH<sub>4</sub> efflux measurements from this new spoke began on July 27, for the chambers LT13 to LT18 and on August 8, for LT19 (in lieu of LT13).



**Figure 3.1:** Illustration of the experimental field set up highlighting the name and long-term chamber (initial chambers are identified by a yellow triangle, the intermediate chamber is identified by a black triangle, and the long-term chambers are identified by an orange diamond).

From July 27 to August 22, the magnitude of the CH<sub>4</sub> effluxes generally increased continuously, even though the injection was terminated on August 17, 2018 (Figure 3.2). The rate CH<sub>4</sub> efflux increase varied based on the chamber. Variations in CH<sub>4</sub> effluxes throughout the day are believed to be influenced by gas accumulation in the subsurface, accompanied by subsequent periodic releases, in-line with observations of previous studies (Cahill et al., 2017; Forde et al., 2018). After August 22, the CH<sub>4</sub> effluxes began to decrease exponentially until they reached non-detectable limits in early September.

These observations are consistent with Archimedes' principle stating that buoyancy forces drive the gas upwards, if a path is available (Frette et al., 1992; Gurevich et al., 1993). However, at the site, movement of gas is believed to be obstructed by capillary barriers within the grain

matrix, causing build-up and lateral spreading of the free phase synthetic natural gas under a confining layer in the saturated zone, as indicated by geophysical data (Cary, 2019). The gas efflux data suggests that, eventually, the pressure build-up due to gas accumulation in the subsurface was sufficient to overcome capillary forces, resulting in the free phase gas to migrate to the surface along preferential pathways, as was observed previously at other sites (Anderson et al., 2009; Forde et al., 2018; Selker et al., 2007; Tomlinson et al., 2003). Once the active injection ceased, the subsurface free phase gas plume maintained sufficient pressure to lead to continued releases at the surface for nearly a week. Subsequently, the free phase gas was no longer able to maintain sufficient pressure to overcome capillary forces, leading to a decline in effluxes until they could no longer be detected at the surface. The results demonstrate that the steady increase and then decrease in CH<sub>4</sub> effluxes was directly related to pressure build-up associated with injection of the synthetic gas.

Table 3.1 presents statistics of the CH<sub>4</sub> efflux ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) data measured using the longterm chambers from June 1 to October 1, 2018. All locations with elevated CH<sub>4</sub> effluxes are located north-west and upgradient of the gas release point. The highly localised elevated CH<sub>4</sub> effluxes and soil gas concentrations are indicative of vertical discontinuities in the top 10 m, providing strong evidence for the existence of preferential gas pathways through the confining layer to the vadose zone. However, there is insufficient data to determine if there was already a natural preferential pathway present prior to commencement of gas injection and the installation of the monitoring network or if this is an artifact of subsurface disturbance due to the installation of groundwater monitoring wells. Nevertheless, irrespective of the nature of the pathway, the observations demonstrate that for low-permeability soils, such as those present at this site, GM will be emitted along preferential pathways and will be highly localized. The data also shows that fugitive emissions may occur upgradient of the injection location, implying that gas can readily migrate against the direction of groundwater flow and may be considerably mobile.

### 3.2.2 CO<sub>2</sub> Effluxes from Long-term Chambers

In every measurement period (prior, during or after injection), the soil CO<sub>2</sub> effluxes measured for all chamber locations follow a diurnal pattern with lower CO<sub>2</sub> effluxes generally occurring at night. Observed CO<sub>2</sub> effluxes did not correlate to the spatial distribution of CH<sub>4</sub> effluxes. There were significant spatial variations of observed CO<sub>2</sub> effluxes during background measurements ranging from 0.13 to 5.02  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> (Table 3.2). Over the entire measurement period CO<sub>2</sub> effluxes ranged from 0.13 to 12.53  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> (Table 3.2). The CO<sub>2</sub> effluxes followed a commonly observed trend, with CO<sub>2</sub> effluxes increase continuously and peaking at the end of July when temperatures are highest (mid-summer) (Fenn et al., 2010; Thierron & Laudelout, 1996; Witkamp, 1966), most likely due to increased root respiration, then decreasing as temperatures decreased (Figure 3.2). A study of well pads with confirmed FG migration in north-east BC reported CO<sub>2</sub> efflux values between 0.5 to 32.0  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> (Forde et al., 2019). Studies conducted in natural environments such as Boreal forests and grasslands of northern Canada have reported CO<sub>2</sub> effluxes from soil respiration to be highly spatially variable and ranging from very low positive effluxes to 14 µmol m<sup>-2</sup> s<sup>-1</sup> (Domisch et al., 2006; Felice et al., 2018; Gulledge & Schimel, 1998; Niinistö et al., 2011; Rayment & Jarvis, 2000; Subke et al., 2009). The CO<sub>2</sub> effluxes measured during this experiment are generally in the range of CO<sub>2</sub> effluxes reported in the literature for natural soil respiration and are lower than CO<sub>2</sub> effluxes reported by Forde et al. (2019).

Similar studies have shown that surface CO<sub>2</sub> effluxes can be used as an indicator for microbially mediated degradation of petroleum hydrocarbons (Molins et al., 2010; Sihota et al.,

2013; Sihota et al., 2011) and the oxidation of CH<sub>4</sub> to CO<sub>2</sub> (Cahill et al., 2017; Forde et al., 2018). CO<sub>2</sub> effluxes are at their highest generally during the period of elevated CH<sub>4</sub> effluxes (Figure 3.2). However, it is not possible to discern if this is due to increased root respiration related to elevated temperatures or a result of CH<sub>4</sub> oxidation. At this site, CO<sub>2</sub> effluxes alone do not provide sufficient evidence for the occurrence of microbially mediated CH<sub>4</sub> oxidation. There are two potential reasons for the lack of sufficient evidence for the oxidation of the hydrocarbons: 1) the natural variability of the CO<sub>2</sub> effluxes from soil respiration makes it difficult to distinguish these effluxes from CO<sub>2</sub> effluxes attributed to CH<sub>4</sub> oxidation and 2) background monitoring of CO<sub>2</sub> effluxes in the subarea of elevated CH<sub>4</sub> effluxes was insufficient to determine a background range of CO<sub>2</sub> efflux values (due to the relocation of chambers into this area after onset of elevated CH<sub>4</sub> effluxes). Given that CH<sub>4</sub> effluxes were mostly below 2.5 µmol m<sup>-2</sup> s<sup>-1</sup> (Figure 3.2 and Table 3.2) and the natural background soil variability of CO<sub>2</sub> effluxes is between 0.13 to 5.02 µmol m<sup>-2</sup> s<sup>-1</sup>, it is not surprising that a clear CO<sub>2</sub> oxidation signature could not be observed.



**Figure 3.2:** (A): The top panel illustrates  $CH_4$  effluxes (µmol m<sup>-2</sup> s<sup>-1</sup>) as a function of time. (B): The bottom panel illustrates the CO<sub>2</sub> effluxes (µmol m<sup>-2</sup> s<sup>-1</sup>) as a function of time. Both (A) and (B) show effluxes from LT6 (chamber located directly above the gas release point), LT17 (10 m north-west of the gas release point), LT18 (13 m north-west of the gas release point) and LT19 (15.6 m north-west of the gas release point). The three chambers; LT17, LT 18 and LT19 account for more than 90% of the total CH<sub>4</sub> effluxes obtained from long-term chambers at the HHFRS.

**Table 3.1:** The statistics (mean, standard deviation, minimum value and maximum value) from the long-term chambers for the  $CO_2$  and  $CH_4$  effluxes (µmol m<sup>-2</sup> s<sup>-1</sup>). There are more than twelve locations below since some long-term chambers were relocated, in one instance twice. In some cases, the mean fluxes are BDL; however, there were fluxes measured and therefore std dev, minimum and maximums are reported.

Chamber	Date Installed (2018)	Date Decomm -issioned (2018)	CH <sub>4</sub> efflux (µmol m <sup>-2</sup> s <sup>-1</sup> )				CO <sub>2</sub> efflux (µmol m <sup>-2</sup> s <sup>-1</sup> )			
			mean	Std. dev.	min	max	mean	Std. dev.	min	max
LT18	26-Jul	2-Oct	0.77	1.03	-1.22	10.88	1.04	0.81	0.00	11.84
LT17	26-Jul	2-Oct	0.22	0.28	-0.63	4.63	1.76	1.23	0.01	10.95
LT19	08-Aug	2-Oct	0.05	0.65	-2.73	13.99	1.32	0.94	0.01	8.29
LT16	26-Jul	2-Oct	0.16	0.11	-0.50	1.00	1.41	0.96	0.12	6.58
LT15	26-Jul	2-Oct	0.08	0.12	-0.09	2.36	3.28	1.76	0.45	12.53
LT13	26-Jul	8-Aug	-0.02	0.06	-0.17	0.17	6.43	1.72	1.81	11.60
LT1	30-May	2-Oct	-0.04	0.15	-1.02	0.30	1.23	0.73	0.01	5.15
LT3	30-May	2-Oct	BDL	0.03	-0.14	0.26	0.98	0.61	0.00	5.40
LT6	30-May	2-Oct	BDL	0.05	-0.16	0.67	2.48	1.44	0.02	9.33
LT4	30-May	2-Oct	BDL	0.05	-0.21	0.37	1.71	1.03	0.03	6.91
LT14	30-May	2-Oct	-0.02	0.04	-0.11	0.22	1.87	1.08	0.07	6.60
LT5	30-May	2-Oct	BDL	0.04	-0.16	0.74	2.27	1.30	0.00	10.63
LT10	30-May	26-Jul	0.01	0.06	-0.04	0.44	0.56	0.31	0.02	2.16
LT11	30-May	26-Jul	BDL	0.01	-0.08	0.10	2.64	1.85	0.28	13.49
LT12	30-May	26-Jul	BDL	0.03	-0.12	0.27	2.00	0.91	0.15	5.36
LT3	30-May	2-Oct	0.01	0.07	-0.14	1.20	3.82	1.76	0.43	12.72
LT7	30-May	26-Jul	BDL	0.05	-0.12	0.63	3.57	1.89	0.68	12.24
LT8	30-May	26-Jul	0.01	0.08	-0.10	0.91	2.34	1.45	0.13	11.37
LT9	30-May	26-Jul	BDL	0.02	-0.09	0.25	2.13	1.12	0.15	6.82

\*BDL = below detection limit. For this the detection limit of 0.01  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> was used.

### 3.3 CH<sub>4</sub> and CO<sub>2</sub> Effluxes from Discrete Spatial Surveys

Spatial surveys conducted prior to the synthetic natural gas injection showed that CH<sub>4</sub> was being taken up into the soil from the atmosphere, with no clear spatial distribution. Following the start of the injection, CH<sub>4</sub> was not detected at the surface during spatial surveys on June 12, June 13, June 14, June 15, June 26, June 27, and June 28, 2018. Above background CH<sub>4</sub> effluxes were first detected during a spatial survey on July 25, six weeks after the injection began. Geophysical measurements indicated that during the first six weeks the gas had migrated a minimum of 16 m laterally, 26 m vertically, and upgradient topographically of the release point (Cary, 2019). For the entire monitoring period from May 31 to October 1, 2018, elevated CH<sub>4</sub> effluxes occurred around MW2, which is located  $\approx 10$  m upgradient topographically form the gas release point, in the opposite direction to groundwater flow and to the north-west of the gas release point. The emergence of the injection gas  $\approx 10$  m away from the gas release point highlights that GM is significantly influenced by subsurface heterogeneities and stratigraphy, resulting in lateral gas transport. The observed up-gradient transport against groundwater flow provides evidence that factors controlling free-phase gas movement include buoyancy forces, capillary trapping and preferential pathways. These observations demonstrate clearly that gas can migrate against the direction of naturally occurring groundwater flow.

The areal extent of elevated CH<sub>4</sub> effluxes is  $\approx 100 \text{ m}^2$  around MW2, which is indicated with a red square in Figure 3.3. Effluxes were greatest on July 27, roughly 6 weeks after the start of the injection. Lower, but still elevated CH<sub>4</sub> effluxes were observed near MW2 on August 11. The CH<sub>4</sub> effluxes increased slightly again when measured on August 28, 11 days after the injection of gas stopped. The CH<sub>4</sub> effluxes vary in magnitude throughout the day, resulting in intermittent emissions (Figure 3.2), likely due to variations in subsurface gas distribution. Therefore, the slightly lower CH<sub>4</sub> effluxes measured during the spatial survey of August 11 are attributed to the variability of natural gas build-up in the subsurface. This variability is also seen in the continuous measurements of the long-term chambers. By September 28, 2018, CH<sub>4</sub> effluxes around MW2 were below detection.

Survey measurements illustrate that on days when significantly elevated  $CH_4$  effluxes were observed higher  $CO_2$  effluxes were typically also exhibited. It was expected that the regions of elevated  $CO_2$  effluxes would coincide with regions of  $CH_4$  effluxes, as was observed by Forde et al. (2018); however, the elevated  $CO_2$  fluxes were not measured at the exact same locations where elevated  $CH_4$  effluxes were observed. Comparing Figure 3.3 and Figure 3.4, it can be seen that highest  $CH_4$  and  $CO_2$  effluxes were observed on July 27. The large spatial variability of  $CO_2$ effluxes across the site make it difficult to characterize and or quantify potential  $CH_4$  oxidation.



**Figure 3.3:** The spatial distribution of  $CH_4$  effluxes (µmol m<sup>-2</sup> s<sup>-1</sup>) taken from survey measurements on June 6 (pre-injection), July 27 (during active injection), August 11 (during active injection), August 18 (post-injection), September 13 (post-injection), September 28 (post-injection), 2018.



**Figure 3.4:** The spatial distribution of  $CO_2$  effluxes (µmol m<sup>-2</sup> s<sup>-1</sup>) taken from survey measurements on June 6 (pre-injection), July 27 (during active injection), August 11 (during active injection), August 18 (post-injection), September 13 (post-injection), September 28 (post-injection), 2018.
## 3.4 Impact of Climate Parameters

## 3.4.1 3.4.1 Barometric Pressure

Throughout the experimental monitoring period from May 31 to October 1, 2018, there was no clear relationship between barometric pressure and CH<sub>4</sub> fluxes. The R-squared value was 0.002204 and this lack of a relationship can be seen in Figure 3.5. Previous studies have suggested that barometric or atmospheric "pumping," the process by which a decrease in barometric pressure would result in the increased upward migration of free phase gas is a controlling transport mechanism influencing how and when gas will break through at the surface (Auer et al., 1996; Forde et al., 2019; Kuang et al., 2013; Massmann & Farrier, 1992; Nilson et al., 1991; Xu et al., 2014). However, at the HHFRS, the effect of atmospheric pumping is limited since the vadose zone is not sufficiently extensive (extending to a depth between 1.5 and 3.0 m bgs), to store large gas volumes (Figure 3.5) necessary for atmospheric pumping. This explains the lack of correlation between CH<sub>4</sub> effluxes and barometric pressure fluctuations.



**Figure 3.5:** Time series of barometric pressure and CH<sub>4</sub> effluxes from the long-term chamber with the highest efflux (LT 18), located 13 m north-west of the gas release point.

### 3.4.2 Precipitation and Soil Moisture Content

Based on literature from landfill studies, precipitation can have varying effects on CO<sub>2</sub> and CH<sub>4</sub> effluxes (Borjesson & Svensson, 1997; Zhang et al., 2013). Increases in soil moisture content by precipitation events, decreases the gas permeability and diffusivity of the soil, potentially reducing surface effluxes of both CH<sub>4</sub> and CO<sub>2</sub> (Boeckx & Van Cleemput, 1996). This reduces the ability of O<sub>2</sub> to enter the vadose zone, which can limit microbially mediated aerobic oxidation of CH<sub>4</sub> and thus, may decrease the proportion of gas efflux that is CO<sub>2</sub> (Klusman & Dick, 2000). On the other hand, extremely dry conditions may limit microbial activity, which can reduce the oxidation of CH<sub>4</sub> and proportion of flux that is CO<sub>2</sub>. An intermediate moisture level between the two extremes is required for most effective respiration in soils and CH<sub>4</sub> oxidation (Gulledge & Schimel, 1998; Jia et al., 2013; Niinistö et al., 2011). Alternatively, rapid changes in soil moisture, as a result of significant precipitation events, may result in temporary increases in CH<sub>4</sub> and CO<sub>2</sub> effluxes, as the subsurface gas is displaced by infiltrating rainwater (Kim et al., 2012; Zhang et al., 2013).

For the purpose of this thesis, rainfall events were deemed to be significant if the intensity was greater than 10mm/hour, these events are highlighted in gray in Figure 3.6. Based on the significant precipitation events highlighted in Figure 3.6, there is no statistical correlation between precipitation events and changes in  $CO_2$  and  $CH_4$ . The significant precipitation events are associated with a change in volumetric water content which suggests that the water is able to infiltrate at least 5 cm into the soil (Figure 3.7). Examining the data suggests that major precipitation events result in measurable increases in the soil volumetric water content and decreases in temperature, which influence both  $CO_2$  and  $CH_4$  effluxes (Figure 3.7), even though the effect is not strong. Specifically, a temporary decline of both  $CO_2$  and  $CH_4$  effluxes during the

major precipitation event on September 9, 2018 can be seen. However, this effect is short-lived and small in comparison to the variations of gas effluxes during the monitoring period. This temporary decline it is likely due to inhibition of gas diffusion and/or temporary entrapment of gas due to the soils approaching fully saturated conditions (Boeckx & Van Cleemput, 1996). The data also suggests that CH<sub>4</sub> effluxes increase with declining soil moisture contents over longer periods of time (Figure 3.7, July 26 - August 25, 2018) (Boeckx & Van Cleemput, 1996; Bogner & Spokas, 1993). It is not clear, however, if this relationship is coincidental, or a direct function of the drying conditions during this period of time.



**Figure 3.6:** (A): Time series of CH<sub>4</sub> efflux ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) from LT18 (the long-term chamber with the highest flux) located 13 m north-west of the gas release point with precipitation (mm. (B): Time series of CO<sub>2</sub> efflux ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) from LT18 (the long-term chamber with the highest flux) located 13 m north-west of the gas release point with precipitation (mm). The three significant precipitation events have been highlighted by a gray band.



**Figure 3.7:** (A): CO<sub>2</sub> efflux ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) from LT18. (B) CH<sub>4</sub> efflux ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) from LT18, the y axis was cropped to better illustrate the change that occurs during the precipitation event. (C): ambient temperature at the site (°C) which has the same pattern as the subsurface soil temperatures but is used in this figure as the ambient temperature datasets is complete. (D) soil volumetric water content (cm<sup>3</sup> cm<sup>-3</sup>) measured 10 cm bgs. (E) daily precipitation (mm). This figure illustrates how increases in precipitation are associated with increases in soil volumetric water content, decreases in temperature and slight and short-lived decreases in CO<sub>2</sub> and CH<sub>4</sub> effluxes.

In order for CO<sub>2</sub> production or CH<sub>4</sub> oxidation in soils to be limited by dry conditions the soil volumetric water content would generally have to be below 0.1 (Davidson et al., 2000; Orchard & Cook, 1983), but this was never observed at the HHFRS (Figure 3.7) and is unlikely to occur in boreal regions.

## 3.4.3 Temperature

Soil respiration is controlled primarily by temperature and moisture but is also impacted by vegetation and substrate quality (Fang & Moncrieff, 2001; Gaumont-Guay et al., 2006, 2009; Kirschbaum, 1995; Niinistö et al., 2011; Rayment & Jarvis, 2000). Isolating the effects of moisture versus temperature is often difficult as they are typically statistically confounded (Davidson et al., 2000).

The temperature effect on soil respiration is usually described as an exponential and Arrhenius kinetic equation (Davidson et al., 2000; Fang & Moncrieff, 2001; Lloyd & Taylor, 1994). The Spearman correlation between temperature and  $CO_2$  efflux was estimated and ranged from 0.47 to 0.81 depending on the long-term chamber location. The only chamber that had a Spearman correlation less than 0.7 was LT18 (13 m north-west of the gas release point), where the largest CH<sub>4</sub> effluxes were measured (Figure 3.7). However, the relatively poor statistical correlation might imply that the CO<sub>2</sub> effluxes at LT18 were affected by increased CH<sub>4</sub> effluxes and abundance, overprinting the temperature effect. Nevertheless, statistical analysis indicates that the majority of variability in CO<sub>2</sub> effluxes can be explained by temperature variations. This statistical correlation can be seen visually in Figure 3.8 and Figure 3.9 using LT6 as an example, where fluctuation in CO<sub>2</sub> effluxes are seen to directly align with fluctuations in temperature.



**Figure 3.8:** Time series of CO<sub>2</sub> efflux ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) from LT6 (chamber above the gas release point) and temperature (°C) with a 10 point running average.



**Figure 3.9:** Time series of CO<sub>2</sub> efflux ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) from LT6 (chamber above the gas release point) and temperature (°C) with exponential fit line in black. The relationship between CO<sub>2</sub> effluxes and temperature is exponential and thus this data fits the trend well.

# 3.4.4 Diel Variations and Wind Speed

Effluxes showed diurnal variations, with more pronounced effects for  $CO_2$ , but also visible effects for CH<sub>4</sub>. At night, when windspeeds reduced to be close to the detection limit of the 3D sonic anemometer (CSAT3B), increased CO<sub>2</sub> and CH<sub>4</sub> concentrations above the soil surface were observed (Figure 3.10, Figure 3.11, and Figure 3.12). This resulted in reduced CO<sub>2</sub> effluxes and CO<sub>2</sub> accumulation in the soil. This leads to increased CO<sub>2</sub> effluxes in the early morning as the stored CO<sub>2</sub> is released when sufficient atmospheric turbulence is re-established. This trend was also observed by Brændholt et al. (2017) and the wind speed variation resulted in more variable CH<sub>4</sub> effluxes. There is a more significant range in CH<sub>4</sub> effluxes at night with maximum effluxes occurring in the evening (Figure 3.10 and Table 3.2). These relationships are illustrated by data in Figure 3.10, Figure 3.11and Figure 3.12.

Although wind is an important physical factor impacting  $CO_2$ , temperature plays a significantly larger role in regulating the soil  $CO_2$  effluxes due to the direct impact on microbial activity which drives the fluxes (Xu et al., 2004). However, wind impacts on atmospheric mixing could have a greater impact on CH<sub>4</sub> effluxes resulting from fugitive CH<sub>4</sub> as it is able to influence the concentration gradients by altering CH<sub>4</sub> concentrations at the surface. In addition, the effect on  $CO_2$  effluxes is likely also impacted by increased root respiration (Fenn et al., 2010).



**Figure 3.10:** (A): CH<sub>4</sub> efflux ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) measured at LT18 (13 m north-west of the gas injection point). (B): wind speed (U) at 1.56 m above the ground. (C): CH<sub>4</sub> concentration (ppm) in the chamber and ambient concentrations. (D): Ambient temperature that is an analogue for soil temperature (°C). Each of these datasets were collected between August 31, to September 5, 2018. All orange dots represent data collected during the day and all blue crosses represent data points collected at night.



**Figure 3.11:** (A):  $CO_2$  efflux (µmol m<sup>-2</sup> s<sup>-1</sup>) from LT5 (1 m South of the gas injection point). (B): wind speed (U) at 1.56 m above the ground. (C):  $CO_2$  concentration (ppm) in the chamber and ambient concentrations (measured from the EC tower). (D): soil temperature and ambient temperature (°C). Each of these datasets were collected between July 9, to July 13, 2018. All orange dots represent data collected during the day and all blue crosses represent data points collected at night.  $CO_2$  efflux varied proportionally to temperature during the day but decreased in magnitude and fluctuated significantly at night when wind speeds were lower.



**Figure 3.12:** (A): CO<sub>2</sub> effluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) against CO<sub>2</sub> concentrations (ppm) for the same data collected between July 9, to July 13, 2018 using long-term chambers. CO<sub>2</sub> concentrations are greater at night and fluxes are lowest during the same period. (B): CH<sub>4</sub> effluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>) against CH<sub>4</sub> concentrations (ppm) for the same data collected between July 28 to August 3, 2018 using long-term chambers. Generally, CH<sub>4</sub> concentrations are greater at night and fluxes are lowest during the same period but there is more variability.

The impact of windspeed on  $CH_4$  effluxes can be more clearly seen in Table 3.2, which illustrates how at night, when wind speeds are lower, both  $CH_4$  effluxes and  $CH_4$  initial concentrations measured in the chamber (equivalent to the atmospheric concentration just above the soil) are consistently higher than the daytime averages in almost all locations. Fluctuations in night-time  $CH_4$  effluxes (with some efflux measurements being greater than the more stable daytime effluxes) are illustrated in Figure 3.10 and Figure 3.12; despite the fact that the figure illustrates generally decreasing  $CH_4$  effluxes over the time period. Peak  $CO_2$  effluxes occur in the early morning when the atmosphere is more stable and stored excess  $CO_2$  is released. In the context of fugitive gas migration, this supports the idea that continuous monitoring is required in order to be able to better understand and accurately quantify leaks via surficial measurements (Forde, 2019).

**Table 3.2:** Average  $CH_4$  efflux (µmol m<sup>-2</sup> s<sup>-1</sup>) and  $CH_4$  concentrations (ppm) from June 1, to October 1, 2018, for each chamber location.

Chamber	CH4 efflux (	(µmol m <sup>-2</sup> s <sup>-1</sup> )	CH <sub>4</sub> concentration (ppm)		
	Day	Night	Day	Night	
LT 6 (Gas release Point)	4.80E-05	3.42E-04	1.9	2.4	
LT19 (15.6m NW)	3.16E-02	6.68E-02	2.7	3.6	
LT18 (13.0m NW)	7.76E-01	6.93E-01	5.3	18.7	
LT17 (10.0m NW)	2.12E-01	2.31E-01	2.3	4.8	
LT16 (7.0m NW)	1.34E-01	1.80E-01	2.1	3.3	
LT15 (5.2m NW)	5.64E-02	9.71E-02	2.0	2.8	
LT14 (2.5m NW)	1.50E-02	-2.21E-02	2.4	3.6	
LT13 (1.0m NW)	-1.56E-02	-1.92E-02	2.2	3.9	
LT3 (3.0m S)	1.68E-03	1.17E-02	1.9	2.3	
LT4 (2.0m S)	7.53E-04	-2.71E-02	1.9	2.7	
LT5 (1.0m S)	1.02E-03	-5.20E-03	1.9	2.5	
LT2 (6.0m S)	1.87E-04	6.86E-04	1.9	2.6	
LT1 (12.0m S)	-4.53E-02	-1.45E-02	2.2	3.4	
LT7 (1.0 E)	1.30E-03	5.83E-03	1.9	2.1	
LT8 (2.0 E)	6.41E-04	6.73E-03	1.9	2.2	
LT9 (3.0 E)	3.82E-04	-8.53E-04	1.9	2.1	
LT10 (6.0 E)	-1.01E-03	1.90E-02	1.9	2.2	
LT 11 (9.0 E)	-2.03E-04	-6.70E-03	1.9	2.1	
LT12 (12.0 E)	7.01E-04	2.73E-03	1.9	2.1	

# 3.5 Comparison to EC Data

A full integration of chamber and EC efflux data is beyond the scope of this thesis. Instead the measured  $CH_4$  effluxes collected from the EC tower are presented (Figure 3.13) and briefly discussed in relation to the effluxes measured with the chamber method.  $CO_2$  effluxes have not

been considered in this comparison, because the EC method fully captures the impact of photosynthesis and respiration, while the chamber measurements performed in this study focused on capturing CO<sub>2</sub> emitted from the soil, which are only partially influenced by photosynthesis effects because when the chamber is open the vegetation in the collar is able to photosynthesize. The use of transparent chambers would enable a chamber to capture the effect of photosynthesis but that was not the goal of this study, as the focus was to attempt to use the chambers to make inferences on subsurface processes. Another key distinction between the two types of measurement systems is that the EC tower obtains a flux for an entire footprint area (Figure 3.14) that varies in time, while the chambers are only able to determine the flux in the 317.8 cm<sup>3</sup> internal area of the collar at select locations. An example of the EC footprint with relative contribution of the surface area to EC efflux can be seen in Figure 3.14. The EC method typically results in averaged efflux values over the footprint area (Figure 3.14), whereas the chamber method measures effluxes at one location.

Figure 3.13 shows long-term efflux measured by the chamber method at selected locations in panel (A) and 30-minute averaged, filtered, EC data in panel (B). Wind conditions at the site generally did not favor transport from the gas release point toward the EC tower. When the EC data was filtered for sufficient atmospheric mixing and wind from the south-east, which allows for transport of gas from the source zone to the tower, reliable data could only be obtained for < 20% of the entire measurement period. To account for this missing data, the data points were linearly interpolated. Data in Figure 3.13 has been interpolated based on available data and results will be elaborated on in Chitra Chopra's MSc thesis (in progress).

Figure 3.13 demonstrates that measurements from both the EC and chamber method show a similar CH<sub>4</sub> efflux distribution over time. For both methods, elevated effluxes were seen towards the end of July and subsequently steadily increased for several weeks. The EC data demonstrates a gentler  $CH_4$  efflux decline (compared to the chamber data) around mid-August; however, this is a function of the integrated nature of the EC data collection. Additional research is required for an integration of the two methods, which is beyond the scope of this thesis.



**Figure 3.13:** (A): CH<sub>4</sub> effluxes (µmol  $m^{-2} s^{-1}$ ) measured from the long-term chambers closest to MW2. (B): CH<sub>4</sub> effluxes (µmol  $m^{-2} s^{-1}$ ) measured using the EC method.



**Figure 3.14:** (A): 3D image of the EC footprint on August 3, 2018 at 6:30pm. (B): a 2D image of the EC footprint on July 9, 2019 and the white dot represents the gas release point. For both images the origin is the location of the EC tower and the distances along the axis are in meters. The colour-bar represents the % contribution of the fluxes on the surface to the total EC efflux.

# 3.6 Estimation of Gas Volume Released to the Atmosphere Based on Long-Term Chamber Measurements

To estimate the volume of the synthetic injection gas (approximated by CH<sub>4</sub>) released to the surface based on the long-term chamber measurements, the representative spatial region of each long-term chamber displaying elevated fluxes needed to be determined (Figure 3.15). Each grid cell in Figure 3.15 has a length and width defined as half the distance between the measurement point and the closest adjacent measurement point in each direction. To calculate areal effluxes, we assume that the measurement obtained from the chamber in the centre of each cell represents the efflux from the entire area covered by the cell.

A comparison of discrete spatial survey measurements to the continuous long-term chamber measurements revealed that the five long-term chambers in the hatched cells of Figure 3.15. (labelled *a* to *e*) account for 32.7% to 46.9% of all CH<sub>4</sub> fluxes measured during the survey measurements.



**Figure 3.15:** A layout of the site in the region with elevated CH<sub>4</sub> effluxes, showing how the site was dived to calculate aerial fluxes.

For each long-term chamber in the hatched region of Figure 3.15, the measured CH<sub>4</sub> efflux in  $\mu mol \ m^{-2}s^{-1}$  is multiplied by the area of the cell to obtain an emission rate in  $\mu mol \ s^{-1}$ . This value is then multiplied by the time interval between measurements (in seconds) to obtain a value in  $\mu mol$ . This molar mass is converted to m<sup>3</sup> (at standard temperature and pressure, STP) by multiplying the value by 22.4 L mol<sup>-1</sup> and dividing it by 1000 L m<sup>3</sup>.

The efflux is calculated as follows:

I. Multiply the CH<sub>4</sub> efflux calculated at a specific chamber by the associated area based on Figure 3.9 to obtain a value in  $\mu mol s^{-1}$ ).

CH<sub>4</sub> efflux  $(\mu mol \ m^{-2} s^{-1}) \times Area \ (m^2) = X \ (\mu mol \ s^{-1})$ 

- II. Multiply this value by the time (s) between each measurement and sum over all measurements to obtain the total number of micro moles.  $X (\mu mol s^{-1}) \times time (s) = Y \mu mol$
- III. Convert from micro moles to moles:

 $Y \mu mol \times 10^6 = Y mol$ 

IV. Convert the quantity from moles to cubic meters:

$$Y \ mol \ \times \frac{22.4 \ L \ mol^{-1}}{1000 \ L \ m^3} = Z \ m^3$$

The above calculation was performed sequentially for each chamber in python using the np.trapz function for two scenarios, where the long-term chambers account for 32.7% and 46.9% of the total CH<sub>4</sub> effluxes coming to the surface. The total flux at the site is then computed by dividing the final results by 0.327 for the first scenario and 0.469 for the second scenario. The results of this integration are displayed in Table 3.3. The np.trapz function in python linearly interpolates data gaps.

**Table 3.3:** Estimation of volume of the injected gas released at the surface (m<sup>3</sup>). The volume is calculated based on

 the corresponding areas in Figure 3.15.

Region	Estimations of the Volume of Injection Gas Detected at The Surface (m <sup>3</sup> )					
corresponding to Figure 3.11	Assuming the Long-Term Chambers Account for 32.7% of Total Fluxes	Assuming the Long-Term Chambers Account for 46.9% of Total Fluxes				
А	1.66	1.15				
В	2.82	1.97				
С	1.33	0.93				
D	0.43	0.30				
Е	0.08	0.05				
Sum	6.32	4.40				

Based on this estimation method, 4.40 m<sup>3</sup> to 6.32 m<sup>3</sup> of the injected gas was emitted at the surface (corresponding to 4.5 to 6.5% of the total gas injected into the subsurface, Table 3.3) between July 27 and September 29, suggesting that most of the gas has remained in the subsurface.

Although this method is the best that can be done in the current scenario using only the chamber method, there are various associated limitations and assumptions. The above calculation only considers data from July 27 to September 29, 2018. Gas that arrived at the surface before July 27 is not accounted for in this calculation. Additionally, the chamber method measures fluxes across a small area of only 317.8 cm<sup>2</sup> and assumes that the measurement from the internal surface area of the collar is representative of the larger surrounding area specified in Figure 3.15. The last assumption is that the survey grid in the area was able to capture majority of effluxes at the surface. With these limitations, it is not possible to accurately assign an error to the estimated volume.

## 3.7 Conclusions

Long-term and survey chambers were used to capture the spatially and temporally variable fugitive CH<sub>4</sub> emissions stemming from the introduced injection gas. The long-term chambers were able to continuously and monitor CO<sub>2</sub> and CH<sub>4</sub> effluxes for selected locations, while the survey chamber

measurements were able to capture spatial efflux distributions across the HHFRS. Efflux measurements revealed that it took almost six weeks for the natural gas to find an imperfection(s) in the confining layer and break through at the surface. Once elevated fluxes were detected at the surface, they continued to increase until one-week post injection, after which they decreased exponentially when presumably, the gas plume was unable to maintain sufficient pressure to drive vertical GM. The trend in chamber effluxes aligns well with data collected using the EC system. There was no correlation between barometric pressure fluctuations and CH<sub>4</sub> effluxes at this site, likely due to the thin vadose zone. Elevated CH<sub>4</sub> effluxes were concentrated in the north-west around monitoring well MW2, suggesting the presence of a preferential pathway in this region. It is not clear whether this pathway was introduced by the installation of MW2 or was present prior to installation of the monitoring network. Nevertheless, irrespective of the origin of the preferential pathway, the observed gas emission pattern shows that at sites covered by low permeability soils, GM is spatially constrained, and the location can be difficult to identify. These findings are in-line with the observations by Forde et al. (2019), who carried out a spatial survey at multiple well pads in north-east BC. The chamber method alone assumed that 4.5 to 6.5 % of the total injected gas was emitted at the surface. This suggests that the geology and confining layer present at this site does result in majority of the gas remaining in the subsurface unless irregularities resulting in preferential pathways are present.

# **Chapter 4: Soil Gas Composition and Isotopic Measurements**

# 4.1 Introduction

This chapter contains the results and interpretation of the composition measurements of soil gas samples collected across the HHFRS, allowing for the stipulation of the migration pathways of the injection gas. The isotopic measurements and results are explored and provide supporting evidence for the fate of the gas in the vadose zone. Finally, the insights provided by the miniRUEDI mass spectrometer are described.

### 4.1.1 4.1.1 Chapter Objectives:

- I. Characterize CH<sub>4</sub> and CO<sub>2</sub> concentrations and concentration gradients in the vadose zone.
- II. Use stable-carbon and stable-hydrogen isotopes to assess CH<sub>4</sub>, C<sub>2</sub> and C<sub>3</sub> oxidation in the vadose zone.
- III. Assess the miniRUEDI's ability to detect trace gases in the field in real time.

## 4.1.2 Soil Gas Sample Overview

A total of thirteen rounds of soil gas samples were collected in 2018 from 22 locations with ports at 0.45 m bgs and 1.15 m bgs and one round of sampling was completed in June 2019. Eleven of the twelve initial long-term chamber locations had a co-located soil gas well. The only long-term chamber location that did not have a co-located soil gas well was the chamber above the gas release point due to a lack of space as a result of nearby collars for survey measurements, long-term chambers and groundwater monitoring wells. Once the initial spoke trending west-east was moved only three new soil gas wells could be installed and co-located with three of the long-term chambers constituting the spoke. Figure 4.1 illustrates the location of each soil gas well and the associated naming convention will be used throughout this chapter.



**Figure 4.1:** Illustration of the experimental field set up highlighting the location of each soil gas well (identified by a purple cross).

## 4.2 Soil Gas Compositional Data

Compositional analysis for all soil gas samples was performed at the University of Calgary Isotope Science Laboratory. Average background soil gas concentrations had CH<sub>4</sub>, C<sub>2</sub> and C<sub>3</sub>, concentrations that were BDL, CO<sub>2</sub> ranged from 0.15 to 2.82 % (v/v) with an average of 1.44  $\pm$ 0.60 % (v/v), N<sub>2</sub> ranged from 77.83 to 79.65 % (v/v) with an average of 78.58  $\pm$  0.54 % (v/v) and O<sub>2</sub> ranged from 16.94 to 20.75 % (v/v) with an average of 19.09  $\pm$  0.90 % (v/v). Since CH<sub>4</sub> was not found in soil gas prior to the gas release, samples that contained CH<sub>4</sub> at concentrations greater than 0.001 % (v/v) (10 ppm) were considered to conclusively contain CH<sub>4</sub> originating from the introduced synthetic natural gas. Elevated concentrations of CH4 were measured in only 29 sample tubes at only five soil gas wells: SG2, SG5, SG15, SG17 and SG18 (Figure 4.2 and Table 4.1).

Tantan	Depth	Date				% (v/v)			
Location	(m bgs)	Collected	Ar	<b>O</b> <sub>2</sub>	<b>N</b> <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	C2	Сз
SG18	1.15	2018-08-15	0.57	8.68	48.85	3.21	34.79	2.66	1.42
SG18	0.45	2018-08-08	0.75	13.85	59.97	2.03	21.32	1.47	0.74
SG18	0.45	2018-08-15	0.69	15.18	63.98	2.02	15.94	1.26	0.71
SG18	0.45	2018-08-24	0.79	18.45	71.24	0.86	7.62	0.62	0.34
SG18	1.15	2018-08-24	0.82	19.07	73.61	0.80	5.05	0.38	0.20
SG18	1.15	2018-09-13	0.87	16.46	76.78	1.13	4.10	0.25	0.15
SG18	0.45	2018-09-13	0.94	17.03	77.66	0.77	3.31	0.17	0.09
SG17	1.15	2018-08-15	0.86	18.82	75.87	1.60	2.44	0.17	0.08
SG17	1.15	2018-08-24	0.91	19.84	76.41	1.08	1.48	0.11	0.06
SG17	1.15	2018-09-13	0.88	19.30	77.82	0.79	1.07	0.06	0.03
SG17	0.45	2018-08-15	0.90	20.11	77.15	0.94	0.64	0.05	0.03
SG17	0.45	2018-09-13	0.89	20.04	77.92	0.36	0.54	0.03	0.02
SG17	1.15	2018-08-08	0.90	20.32	77.74	0.50	0.49	0.03	0.02
SG17	0.45	2018-08-24	0.89	20.74	77.75	0.39	0.22	0.02	0.01
SG15	1.15	2018-08-08	0.87	18.01	77.64	3.29	0.15	0.01	0.01
SG17	0.45	2018-08-08	0.86	20.55	77.80	0.27	0.12	0.01	0.01
SG15	1.15	2018-09-13	0.92	19.58	78.05	1.08	0.06	0.00	0.00
SG15	1.15	2018-08-15	0.87	18.79	77.57	2.55	0.04	0.00	0.00
SG15	0.45	2018-09-13	0.91	20.13	78.26	0.53	0.03	0.00	0.00
SG15	1.15	2018-08-24	0.94	19.95	77.47	1.66	0.01	0.00	0.00
SG5	1.15	2018-08-24	0.89	20.63	77.76	0.65	0.01	0.00	0.00
SG2	0.45	2018-08-24	0.88	20.43	77.47	1.03	0.01	0.00	0.00
SG15	0.45	2018-08-24	0.95	20.58	77.84	0.49	0.00	0.00	0.00
SG15	0.45	2018-08-08	0.90	20.50	78.16	0.51	0.00	0.00	0.00
SG2	0.45	2018-08-15	0.89	20.52	77.92	0.59	0.00	0.00	0.00
SG5	0.45	2018-09-13	0.90	19.11	78.83	0.98	0.00	0.00	0.00
SG4	0.45	2018-08-08	0.90	18.67	77.03	3.69	0.00	0.00	0.00
SG2	0.45	2018-08-24	0.91	20.21	77.43	1.28	0.00	0.00	0.00
SG15	1.15	2018-08-24	0.87	20.55	77.78	0.79	0.00	0.00	0.00

**Table 4.1:** Soil gas concentration data collected during and after the synthetic natural gas release. The samples were run at the University of Calgary ISL and are organised in descending order of CH<sub>4</sub> concentration. The entire dataset is available in Appendix C.

\*BDL = below detection limit

First, I will focus on the soil gas composition data from SG15, SG17 and SG18 as they generally follow similar trends and were all installed on July 25, 2018. Samples collected from SG15, SG17 and SG18 contained the highest concentrations of CH<sub>4</sub> (larger by an order of magnitude compared to SG2 and SG5) and account for roughly 80% of all samples with elevated CH<sub>4</sub> (Figure 4.2. and Table 4.1). This is in agreement with the soil efflux data presented in chapter 3, since the most elevated CH<sub>4</sub> effluxes were also measured at the co-located long-term chambers.

SG15 was 6.9 m, LT17 was 3.0 m and LT18 was 3.1 m away from MW2. Soil gas wells and long-term chambers could not be placed closer to MW2 as there was a visible 1.5 to 2.5 m region where bentonite was present on the ground surface, which was believed to obstruct any potential soil gas effluxes. Therefore, LT17 and LT18 were placed 3.0 m away from the MW2 wellhead.



Figure 4.2: Illustration of the experimental field site set up. Soil gas wells where elevated CH<sub>4</sub> was detected have

been circled.

At these locations, the highest concentrations of CH<sub>4</sub> and C<sub>2</sub> were detected between August 8 and 17, 2018, while gas was still being actively injected into the subsurface. The hydrocarbon concentrations were greater in samples collected at 1.15 m bgs compared to those collected at 0.45 m bgs (except SG18 on August 24, 2018); providing evidence that in this region gas migrated from deeper in the subsurface to the surface. The highly localised nature of elevated CH<sub>4</sub> soil gas concentrations in addition to upward migration of the gas (demonstrated by the concentration gradient) provides additional evidence for the existence of preferential pathways through the confining layer and the vadose zone, as was seen in previous studies (Gerard et al., 2014; McCray & Falta, 1996; Selker et al., 2007). Additionally, Figure 4.3 generally illustrates that in samples with elevated hydrocarbons present, there was a significant decrease in both O<sub>2</sub> and N<sub>2</sub>. The decrease in  $N_2$  is a result of the hydrocarbon displacement due to the upward transport of the injection gas (Amos et al., 2005). The percentage decrease of  $O_2$  is greater than that of  $N_2$  providing evidence that the decrease in O<sub>2</sub> is due to microbially mediated aerobic oxidation. Microbial oxidation in the vadose zone is further supported by isotopic data. Furthermore, peak CO<sub>2</sub> concentrations aligned with peak CH<sub>4</sub> concentrations. However, based on this concentration data alone, it is not possible to determine if this elevated CO<sub>2</sub> has been influenced by CH<sub>4</sub> oxidation because; 1) background  $CO_2$  concentrations at the site are spatially variable and elevated, 2) sufficient long-term subsurface  $CO_2$  monitoring in this area was logistically not possible, 3)  $CO_2$ subsurface concentrations are similar to other soil gas wells that did not have elevated CH<sub>4</sub>, and 4) near surface CO<sub>2</sub> concentrations tend to be at their highest concentrations during that period of the year due to the influence of ambient temperature on root respiration (Risk et al., 2002).



**Figure 4.3:** The above figure illustrates the % (v/v) for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, and N<sub>2</sub>, for SG18 SG17 and SG15. (A) illustrates the % (v/v) of CH<sub>4</sub> collected at SG18. (B) illustrates the % (v/v) of C<sub>2</sub>H<sub>6</sub> collected at SG18. (C) illustrates the % (v/v) of CO<sub>2</sub> collected at SG18. (D) illustrates the % (v/v) of N<sub>2</sub> at SG18. (E) illustrates the % (v/v) of CH<sub>4</sub> collected at SG17. (F) illustrates the % (v/v) of C<sub>2</sub>H<sub>6</sub> collected at SG17. (G) illustrates the % (v/v) of CO<sub>2</sub> collected at SG15. (J) illustrates the % (v/v) of C<sub>2</sub>H<sub>6</sub> collected at SG17. (I) illustrates the % (v/v) of CH<sub>4</sub> collected at SG15. (L) illustrates the % (v/v) of CO<sub>2</sub> collected at SG15. (L) illustrates the % (v/v) of N<sub>2</sub> collected at SG15. (L) illustrates the % (v/v) of N<sub>2</sub> collected at SG15. (L) illustrates the % (v/v) of N<sub>2</sub> collected at SG15.

This next section will focus on soil gas composition data from SG2 and SG5. In Figure 4.4, unlike for the soil gas wells located in the north-west (SG15, SG17, SG18) of the site, the highest concentrations of CH<sub>4</sub> and C<sub>2</sub> were measured post-injection. The increase in CH<sub>4</sub> and C<sub>2</sub> concentrations observed over the nine-day period from August 15, 2018, (period of active injection) to August 24, 2018, (period of post injection) is close to an order of magnitude for both locations. In this case, despite not being detected at the surface by the co-located long-term

chambers, the gas migrated a minimum of 6 m south of the gas release point horizontally, and 25 m vertically. At SG5 the greatest concentrations of CH<sub>4</sub> and C<sub>2</sub> were measured from the sampling port 1.15m bgs. This is consistent with samples from SG15, SG17 and SG18 suggesting a dominant gas migration pathway from deeper in the subsurface to the surface. However, at SG2 the greatest concentrations of CH<sub>4</sub> and C<sub>2</sub> were measured from the sampling port at 0.45m bgs. There is a known sand lens located at  $\approx 0.50$  m bgs that is relatively continuous throughout the centre of the HHFRS. Thus, a potential explanation the for increased concentration at 0.45 m bgs at only SG2, is that the gas migrated horizontally through the known sand lens from a neighbouring location and intersected the SG2 shallow gas sampling port, as opposed to be migrating through relatively vertical preferential pathways as seen at the other soil gas wells.

The arrival of injected gas at SG2 and SG5 is indicative of the presence or development of a alternative preferential gas migration pathway(s), unrelated to GM in the vicinity of SG15, SG17 and SG18, which subsided during this period of time.



**Figure 4.4:** The above figure illustrates the % (v/v) for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, and N<sub>2</sub>, for the two soil gas wells south of the gas release point. (A) illustrates the % (v/v) of CH4 collected at SG5. (B) illustrates the % (v/v) of C<sub>2</sub>H<sub>6</sub> collected at SG5. (C) illustrates the % (v/v) of CO<sub>2</sub> collected at SG5. Panel (D) illustrates the % (v/v) of N<sub>2</sub> collected at SG5. Panel (E) illustrates the % (v/v) of CH<sub>4</sub> collected at SG2. Panel (F) illustrates the % (v/v) of C<sub>2</sub>H<sub>6</sub> collected at SG2. Panel (G) illustrates the % (v/v) of CO<sub>2</sub> collected at SG2. Panel (H) illustrates the % (v/v) of N<sub>2</sub> collected at SG2.

# 4.3 Soil Gas Isotopic Data

Stable carbon and hydrogen isotopes are able to provide evidence regarding the fate of the injection gas in the subsurface as well as the origin of the gas (Whiticar, 1999). Only 16 samples from SG15, SG17 and SG18 had sufficient concentrations (> 0.1 % (v/v) of CH<sub>4</sub>) to analyse for stable-carbon isotope ratios on the CH<sub>4</sub>, and only samples from SG17 and SG18 had sufficient concentrations to analyse for stable-hydrogen ratios. Samples with > 0.1 % (v/v) of CH<sub>4</sub> also contained elevated concentrations of  $C_2$  and  $C_3$ . Due to the low CH<sub>4</sub> background concentrations in all soil gas wells, it was not possible to determine background  $\delta^{13}$ C-CH<sub>4</sub> and  $\delta^{2}$ H-CH<sub>4</sub> values for the field site. Thermogenic CH<sub>4</sub> is typically enriched in <sup>13</sup>C relative to biogenic CH<sub>4</sub> (Whiticar, 1999). As a result, thermogenic CH<sub>4</sub> has a  $\delta^{13}$ C-CH<sub>4</sub> (‰ PDB) of  $\approx$  -50‰ to -20‰ and  $\delta^{2}$ H-CH<sub>4</sub> (‰ SMOW) values of  $\approx$  -275% to -100% (Whiticar, 1999). The isotope values of the synthetic natural injection gas ( $\delta^{13}$ C-CH<sub>4</sub> = -40.3‰ and  $\delta^{2}$ H-CH<sub>4</sub> = -151.6‰) fall into the thermogenic range (see Table 4.2). Although similar in nature, isotope values of the gas samples collected from gas monitoring wells SG15, SG17 and SG18 are less negative than observed in the injection gas ( $\delta^{13}$ C-CH<sub>4</sub> ranges between -31.8‰ and -19.3‰, while  $\delta^2$ H-CH<sub>4</sub> varies between -144.5‰ and -89.3‰, see Table 4.3). Considering that there are no other significant sources of CH<sub>4</sub> at the site, as evidenced by the survey on gas composition (see above), the isotopic signature observed in samples from gas monitoring wells is indicative of microbially mediated CH<sub>4</sub> oxidation (Whiticar, 1999).

**Table 4.2:** Stable  $\delta^{13}$ C and  $\delta^{2}$ H isotope values of CH<sub>4</sub>, C1, C2, C3 and CO<sub>2</sub> and the Bernard ratio of the injection gas.

Sample	δ <sup>13</sup> C-CH <sub>4</sub>	δ <sup>2</sup> H-CH <sub>4</sub>	δ <sup>13</sup> C- C <sub>2</sub>	δ <sup>2</sup> H- C <sub>2</sub>	δ <sup>13</sup> C-C <sub>3</sub>	δ <sup>2</sup> H -C <sub>3</sub>	δ <sup>13</sup> C-	C <sub>1</sub> /
Name	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	CO <sub>2</sub> (‰)	(C <sub>2</sub> +C <sub>3</sub> )
Injection Gas	-40.28	-154.64	-28.91	-111.37	-33.31	-187.14	-37.41	6.54

Soil Gas	Depth	Date	δ <sup>13</sup> C-CH <sub>4</sub>	δ <sup>2</sup> H-CH <sub>4</sub>	δ <sup>13</sup> C- C <sub>2</sub>	δ <sup>2</sup> H- C <sub>2</sub>	δ <sup>13</sup> C-	δ²Η -	δ <sup>13</sup> C-
Well	(m bgs)	(2018)	(‰)	(‰)	(‰)	(‰)	C3 (‰)	C3 (‰)	CO <sub>2</sub> (‰)
SG18	1.15	08-15	-27.71	-140.38	-24.79	-104.55	-30.87	-184.01	-25.72
SG18	0.45	08-08	-31.76	-144.21	-25.47	-105.18	-30.91	-182.10	-27.40
SG18	0.45	08-15	-26.83	-141.47	-23.15	-102.31	-29.98	-182.98	-27.56
SG18	0.45	08-24	-28.21	-144.15	-23.59	-101.03	-29.86	-181.45	-26.13
SG18	1.15	08-24	-31.53	-141.80	-25.11	-103.89	-30.79	-185.89	-26.50
SG18	1.15	09-13	-25.90	-119.01	-21.34	-98.88	-28.18	-173.57	-26.06
SG18	0.45	09-13	-24.27	-121.76	-21.36	-97.20	-28.32	-176.00	-26.59
SG17	1.15	08-15	-30.16	-110.24	-24.09	-94.70	-30.03		-26.21
SG17	1.15	08-24	-24.15	-108.09	-22.79		-29.92		-23.97
SG17	1.15	09-13	-30.82	-114.29	-25.13		-30.59		-26.18
SG17	0.45	08-15	-23.43	-89.39					-24.09
SG17	0.45	09-13	-25.57	-101.44					-23.86
SG17	1.15	08-08	-29.82	-114.46					-26.05
SG17	0.45	08-24	-30.45	-96.00					-23.32
SG15	1.15	08-08	-19.32						-23.43
SG17	0.45	08-08	-25.81						-24.81

**Table 4.3: :** Stable  $\delta^{13}$ C and  $\delta^{2}$ H isotope values of CH<sub>4</sub>, C1, C2, C3 and CO2 for samples collected from SG15, SG17 and SG18.

The general equation for aerobic methane oxidation is (Coleman et al., 1981):

$$^{12}CH_4 + 2O_2 \rightarrow n^{12}CO_2 + (1 - n) * (cell \, carbon) + 2H_2O$$
 (Equation 4.1)

This reaction proceeds for both <sup>12</sup>C and <sup>13</sup>C, with faster rates for the <sup>12</sup>C. The  $\delta^{13}$ C-CH<sub>4</sub> values obtained were on average  $\approx$  -27‰ (Figure 4.5. and Table 4.3), which is the result of an enrichment of  $\delta^{13}$ C in CH<sub>4</sub> due to the kinetic isotope effect which results in the preferential selection of  $\delta^{12}$ C during microbial oxidation (Alperin et al, 1988; Whiticar, 1999; Whiticar et al., 1986). The isotopic data confirms the occurrence of aerobic oxidation that could not be identified via gas effluxes or soil gas concentration measurements (Figure 4.5).

Gas samples that have the greatest concentrations of CH<sub>4</sub>, corresponded to periods when the greatest CH<sub>4</sub> effluxes were observed at the surface. Additionally, samples with higher CH<sub>4</sub> concentrations (and therefore surface effluxes) result in  $\delta^{13}$ C-CH<sub>4</sub> values more similar to the injection gas than samples with lower CH<sub>4</sub> concentrations. This illustrates that during periods of high efflux, a smaller percentage of the gas is able to undergo aerobic oxidation compared to lower efflux conditions. This phenomenon was observed in similar experiments by Forde et al. (2018).

The average  $\delta^2$ H-CH<sub>4</sub> values of the measured samples is -120‰, which is also indicative of microbially mediated CH<sub>4</sub> oxidation, leading to an enrichment of  $\delta^2$ H in CH<sub>4</sub> due to the kinetic isotope effect, similar to the stable-carbon isotopes (Coleman et al., 1981; Feisthauer et al., 2011; Whiticar, 1999). There is no correlation in  $\delta^{13}$ C-CH<sub>4</sub> and  $\delta^2$ H-CH<sub>4</sub> values associated with date collected or depth, suggesting that the gas well location is the main influencing factor (Figure 4.5). Unfortunately, without knowledge of the subsurface microbial community and incubation experiments, it is not possible to infer CH<sub>4</sub> oxidation rates.



**Figure 4.5:**  $\delta^{13}$ C-CH<sub>4</sub> plotted against the  $\delta^{2}$ H-CH<sub>4</sub> for the soil gas samples with sufficient concentration sorted by soil gas well. The samples with the highest concentrations have been circled. No samples from SG15 had sufficient concentrations to analyse for  $\delta^{2}$ H-CH<sub>4</sub>.

Similarly, isotopic data for C<sub>2</sub> and C<sub>3</sub> hydrocarbons (both  $\delta^{13}$ C and  $\delta^{2}$ H) are also indicative of microbial hydrocarbon oxidation, showing enrichment of the heavier isotopes in the soil gas samples for C<sub>2</sub> and C<sub>3</sub> (Figure 4.6.), relative to the injection gas (Kinnaman et al., 2007; Singh et al., 2017). SG17 and SG18 are roughly equidistant from MW2 but only SG18 had samples sufficiently elevated hydrocarbon concentrations for isotopic analysis (with the exception of one sample from SG17).



**Figure 4.6:** (A)  $\delta^{13}$ C-C<sub>2</sub> plotted against the  $\delta^{2}$ H-C<sub>2</sub>. (B)  $\delta^{13}$ C-C<sub>3</sub> plotted against the  $\delta^{2}$ H-C<sub>3</sub> for the soil gas samples with sufficient concentration sorted by soil gas well.

Although it was not possible to measure background  $\delta^{13}$ C for CH<sub>4</sub> due to insufficient concentrations, it was possible to measure background  $\delta^{13}$ C-CO<sub>2</sub>. Average background  $\delta^{13}$ C-CO<sub>2</sub> values for the soil gas samples was -23.9 ‰, the  $\delta^{13}$ C-CO<sub>2</sub> value for the injection gas is -37.4 ‰ and the average the  $\delta^{13}$ C-CO<sub>2</sub> value for samples with elevated CH<sub>4</sub> is -25.6 ‰ (Table 4.2 and Table 4.3). Based on Equation 4.1 it would be expected that gas samples would be enriched in  $\delta^{12}$ C in CO<sub>2</sub> because the microbial degradation of CH<sub>4</sub> preferentially consumes <sup>12</sup>C from the CH<sub>4</sub> and produces CO<sub>2</sub> that is enriched in <sup>12</sup>C (Coleman et al., 1981; Whiticar, 1999; Whiticar et al., 1986). However, only a slight enrichment of <sup>12</sup>C can be inferred from the  $\delta^{13}$ C-CO<sub>2</sub> values, indicating that CO<sub>2</sub> concentrations in soil gas are dominated by CO<sub>2</sub> originating from soil respiration. Similar to the effect of oxidation, mixing between the injection gas and the surrounding background soil gas should also lead to more negative  $\delta^{13}$ C-CO<sub>2</sub> values in the soil gas samples, confirming that the effect of CO<sub>2</sub> originating directly from the injection gas or produced from oxidation of CH<sub>4</sub> in the injection gas is relatively limited (Figure 4.7).



**Figure 4.7:**  $\delta^{13}$ C-CO<sub>2</sub> plotted against  $\delta^{13}$ C-CH<sub>4</sub> for the soil gas samples with sufficient concentrations sorted by soil gas well, isotopic signature of injection gas is also provided.

A modified Bernard diagram is typically used to evaluate the origin of natural gas (Bernard et al., 1978), but can also be used to interpret the compositional and isotopic changes due to

oxidation of hydrocarbons. Figure 4.8 presents a Bernard diagram illustrating the relationship of the gas samples collected from the gas observation wells to the injection gas. The gas samples collected from the monitoring wells do not show any trend relative to depth of collection, location or date collected (Figure 4.8). The collected gas samples are drier and contain relatively more CH<sub>4</sub> overall in comparison to the injection gas. This is most likely a result of the preferential dissolution of C<sub>2</sub> and C<sub>3</sub> into groundwater. A similar trend of increased dryness was observed in the controlled release experiment at the Canadian Forces Borden, ON (Cahill et al., 2017). The vertical shift of the Bernard ratio (Figure 4.8) is indicative of GM, as the gas had to travel 30 m to reach the gas monitoring wells. The horizontal shift in Figure 4.8. is due to the enrichment of  $\delta^{13}$ C in the CH<sub>4</sub> as a result of methane oxidation (Bernard et al., 1978; Coleman et al., 1981; Whiticar, 1999).



Figure 4.8: Bernard ratios (C<sub>1</sub>/(C<sub>2</sub>+C<sub>3</sub>) plotted against the  $\delta^{13}$ C-CH<sub>4</sub> for the soil gas samples with sufficient concentrations sorted by soil gas well.

Ultimately, the isotopic data provides a definitive line of evidence for microbial oxidation of CH<sub>4</sub>, C<sub>2</sub> and C<sub>3</sub> in the vadose zone.

## 4.4 Use of the MiniRUEDI

The miniRUEDI (Brennwald et al., 2016) was used at the HHFRS prior to, during, and following the injection (in June, July, and August, 2018). The main purpose of using the instrument was to detect He concentrations in real time in the field, since He was utilized as a gas tracer in this study. In addition, the instrument allowed to provide real time concentration estimates for Ar, Kr, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>3</sub> (it is unable to conclusively detect C<sub>2</sub>). The compositions of the injection gas, typical gas from the Montney formation and air are summarized in Table 4.4.

**Table 4.4:** Gas composition of the synthetic injection gas (% v/v), the average formation gas of the Montney (% v/v)and air (% v/v). Adapted from Cahill et al., (2019).

Gas	Injection Gas (%v/v)	Formation Gas (% v/v)	Air (% v/v)
CH <sub>4</sub>	85	85	0.0002
C <sub>2</sub> H <sub>6</sub>	8	8	< 0.000001
C3H8	5	3	< 0.000001
CO <sub>2</sub>	1	0.1	0.04
He	0.5	0.01	0.0005
$N_2$	0.5	0.2	78
$O_2$	0	0	21
Ar	0	0	0.9

In late July, approximately six weeks after the injection began, the miniRUEDI detected elevated levels of CH<sub>4</sub>, C<sub>3</sub> and He at MW2, both as a free phase gas and dissolved in the groundwater. Subsequent measurements of soil gas efflux adjacent to well MW2 also showed above background CH<sub>4</sub> effluxes (see Chapter 3). The detection of the injected gas in soil gas ports and as elevated CH<sub>4</sub> surface effluxes was constrained to an area of approximately 100 m<sup>2</sup> around MW2. Once all the data was compiled, the miniRUEDI was used to analyze selected samples (containing elevated CH<sub>4</sub>) to determine He concentrations.

Soil gas samples in the exetainer vials were analysed with the miniRUEDI using the He calibration range 0-1000 ppm, since most samples did not exceed 1000 ppm of He (with the exception of a single sample). All soil gas samples that contained  $CH_4 > 0.01 \%$  (v/v) (factor of 50 times larger than atmospheric concentrations) also contained elevated He, ranging from 15 to 1187 ppm (a factor of 3 to  $\approx 237$  times larger than atmospheric concentrations) (Table 4.5). A linear regression between the He concentrations (measured by the miniRUEDI) and CH<sub>4</sub> concentrations (measured by the University of Calgary ISL) for these samples produced an R<sup>2</sup> value of 0.89 (Figure 4.9).

In the synthetic injection gas, the CH<sub>4</sub>/He ratio was 170. The ratio of CH<sub>4</sub> to He was calculated by subtracting the atmospheric concentration of each gas:

$$(CH_4/He)_{ratio} = (CH_{4,meas} - CH_{4,air}) / (He_{meas} - He_{air})$$
(Equation 4.2)

Since CH<sub>4</sub> and He concentrations are low in air, this ratio essentially presents the CH<sub>4</sub>/He ratio in the sample. In samples where significant injection gas was detected (those containing at least 0.5 % (v/v) CH<sub>4</sub>), the CH<sub>4</sub>/He ratio was similar to that of the synthetic injection gas (170) or showed an elevated CH<sub>4</sub>/He ratio (Table 4.5).

**Table 4.5:** Location, depth, and date of sample collection, concentrations of Ar,  $O_2$ ,  $N_2$ ,  $CO_2$ , C1, C2 and C3 (% v/v) measured by the University of Calgary Isotope Science Laboratory, the He concentrations (ppm) measured by the miniRUEDI and the CH<sub>4</sub>/He ratio.

Location	Depth	Date	% v/v				Не	(CH <sub>4</sub> /He)
Location	(m bgs)	(2018)	CO <sub>2</sub>	C1	C2	C3	(ppm)	ratio
SG18	1.15	08-15	3.205	34.788	2.662	1.417	998	350
SG18	0.45	08-12	2.034	21.316	1.474	0.737	1187	180
SG18	0.45	08-15	2.022	15.937	1.262	0.709	545	296
SG18	0.45	08-24	0.864	7.623	0.622	0.342	357	217
SG18	1.15	08-24	0.795	5.051	0.379	0.202	275	187
SG18	1.15	09-15	1.125	4.104	0.250	0.145	112	383
SG18	0.45	09-15	0.773	3.313	0.170	0.085	105	333
SG17	1.15	08-15	1.603	2.441	0.169	0.084	77	338
SG17	1.15	08-24	1.077	1.475	0.109	0.060	22	863
SG17	1.15	09-15	0.788	1.070	0.061	0.031	65	180
SG17	0.45	08-15	0.940	0.644	0.050	0.028	25	319
SG17	0.45	09-15	0.355	0.538	0.034	0.017	21	336
SG17	1.15	08-12	0.497	0.487	0.034	0.019	35	163
SG17	0.45	08-24	0.385	0.218	0.016	0.010	41	60
SG15	1.15	08-12	3.288	0.149	0.009	0.007	22	87
SG17	0.45	08-12	0.265	0.118	0.009	0.006	32	44
SG15	1.15	09-15	1.077	0.062	0.002	0.002	15	64
SG15	1.15	08-15	2.553	0.040	0.002	0.004	13	50
SG15	0.45	09-15	0.532	0.029	0.001	0.001	12	44
SG15	1.15	08-24	1.658	0.010	0.001	0.002	6	343



**Figure 4.9:** The CH<sub>4</sub> (% v/v) measured by the University of Calgary Isotope Science Laboratory, against the He concentrations (ppm) measured by the miniRUEDI. A linear regression of the data gives and r-squared value of 0.89.

Prior to the experiment it was expected that there would be excess He compared to CH<sub>4</sub> in the final samples (i.e. (CH<sub>4</sub>/He) ratio < 170), since He is expected to migrate upward more rapidly. More rapid upward migration is expected because He dissolves less readily into groundwater than CH<sub>4</sub> due to its low solubility, approximately a factor of 4 lower than the solubility of CH<sub>4</sub> (Lundegard & Johnson, 2006; Neumann et al., 2008; Rumble et al., 2019). However, almost all of the collected gas samples contain elevated CH<sub>4</sub> relative to He with an average ratio of CH<sub>4</sub>/He = 240. Despite the elevated average CH<sub>4</sub>/He ratio, Figure 4.10 does illustrate that several samples are relatively close to the injection gas CH<sub>4</sub>/He ratio.


**Figure 4.10:** CH<sub>4</sub>/He ratios plotted against the CH<sub>4</sub> (% v/v) as measured by the University of Calgary ISL. The dotted line represents the ratio of CH<sub>4</sub>/He of the injection gas. Most gas samples are characterized by an elevated CH<sub>4</sub>/He ratio relative to that of the injection gas.

Figure 4.11 illustrates the CH<sub>4</sub>/He ratio color-coded by collection depth for SG15, SG17 and SG18 as a function of time. SG17 and SG18 are both  $\approx$  3 m away from MW2 and demonstrate similar temporal trends in CH<sub>4</sub>/He ratios (Figure 4.11). At SG17 and SG18, peak CH<sub>4</sub> soil gas concentrations occur mid-August (during active injection of the synthetic gas) coinciding with peak CH<sub>4</sub>/He ratios (Figure 4.11) and gas fluxes. There is no apparent depth trend related to the CH<sub>4</sub>/He ratio for SG17 and SG18 (Figure 4.11). For SG15 (located 6.9 m away from MW2, Figure 4.11), the CH<sub>4</sub>/He ratio trend is different and is most likely affected by the increased distance away from primary preferential GM pathways. For SG15, CH<sub>4</sub> is only present in sufficient concentrations in samples collected from 1.15 m bgs until September 14.



**Figure 4.11:** (A) CH<sub>4</sub>/He ratio for SG17 located 3.0 m away from MW2 as a function of time. (B) CH<sub>4</sub>/He ratio for SG18 located 3.1 m away from MW2 as a function of time. (C) CH<sub>4</sub>/He ratio for SG15 located 6.0 m away from MW2 as a function of time. In (A) the sample collected on August 14, with a CH<sub>4</sub>/He ratio > 800 was omitted.

The reason for the elevated CH<sub>4</sub>/He ratio is not due to biases introduced during sample storage, including loss of He by diffusion through the glass or septa, since test samples were run 6 months apart and the same He concentrations were achieved both times. Since the diffusion coefficient of He in water is larger than that of CH<sub>4</sub> by a factor of approximately 3 (Rumble et al., 2019), the effect of the difference in gas solubility is mediated at least partially, since He is able

to spread laterally more readily following its dissolution into groundwater relative to  $CH_4$ . In addition, the average  $CH_4$ /He ratio in the samples (240) is relatively close to the ratio in the injected gas (170). The ratio between  $CH_4$ /He in the gas samples and  $CH_4$ /He in the injection gas is 1.4.

Overall, these results are confirmatory that the gas collected in the gas monitoring wells originates from the injection gas. CH<sub>4</sub>/He ratios also indicate that CH<sub>4</sub> oxidation was relatively limited, which is somewhat contradictory to the results from the isotopic analysis. However, it must be acknowledged that both gases are affected by multiple processes during upward and lateral migration, and the cumulative effect of these processes is difficult to decipher with certainty.

#### 4.5 Conclusions

Following the synthetic natural gas injection, elevated CH<sub>4</sub> concentrations were detected at five soil gas wells: three were located in the north-west (SG15, SG17 and SG19) co-located with the long-term chambers that detected elevated CH<sub>4</sub> effluxes at the surface, and two wells were located to the south (SG2 and SG5). Samples from the wells in the north-west, around MW2, produced the highest subsurface concentrations of hydrocarbons, with peak concentrations occurring during the period of active gas injection. These wells showed CH<sub>4</sub> concentrations that increased with depth. These observations suggest that there was a primary preferential pathway in this region of the site caused by imperfections in the confining layer, allowing CH<sub>4</sub> to migrate upward to the surface. The occurrence of gas migration to the surface was supported by the miniRUEDI CH<sub>4</sub>/He ratio data that confirmed the presence of the injection gas at the three soil gas wells in the north-west.

In addition, isotopic analysis of stable C and H isotopes provided evidence that, in the vadose zone, CH<sub>4</sub>, C<sub>2</sub> and C<sub>3</sub> were partially oxidized. Locations with higher CH<sub>4</sub>, C<sub>2</sub> and C<sub>3</sub>

concentrations and fluxes showed a less oxidized isotopic signal, suggesting shorter residence times and less oxidation.  $CH_4$ ,  $C_2$  and  $C_3$ , detected near the surface was ultimately drier and isotopically heavier than the injected gas confirming migration and hydrocarbon oxidation of the injected gas.

Once the system as a whole no longer experienced a pressure build-up due to gas injection, less gas was able to break through to the surface in the north-west; however, the injection gas was later detected in much lower concentrations at SG2 and SG5. It appears that the injected gas continued to migrate along alternative pathways that resulted in more significant horizontal migration relative to vertical. The CH<sub>4</sub> efflux measurements were not able to pick up a signal of elevated CH<sub>4</sub> near the injection release point.

In summary, the soil gas data allowed to make inferences on: 1) the location of primary preferential pathways in the vicinity of MW2, 2) the main direction of injection gas migration, as it moved from the subsurface to the surface, 3) CH<sub>4</sub>, C<sub>2</sub> and C<sub>3</sub> was oxidised partially in the vadose zone and 4) once the injection ceased, the gas plume continued to migrate using alternative migration pathways.

The data did not provide conclusive evidence on the nature of the migration pathways and whether the pathways were present prior to installation of the monitoring network or developed due to well installation. In any case, the data conclusively shows that migration pathways, whether natural or man-made, lead to highly localized gas emissions at the surface with additional evidence that migration pathways may evolve over time.

### **Chapter 5: Conclusion**

This thesis focused on characterizing fugitive GM as part of a multidisciplinary controlled release experiment by monitoring gas effluxes across the land-surface-atmosphere boundary, and gas composition in the underlying near-surface soil using a gas-flux chamber method and gassampling wells, respectively.

Large portions of north-east BC, where the majority of British Columbia's current oil and gas development is located, have an overlying silt-clay-diamict layer with low porosity and permeability. Under these conditions, it is expected that it would be difficult for any FG emissions to break through at the surface. While GM is largely driven by buoyancy forces due to gas and pore water density differences (Frette et al., 1992), anisotropy and heterogeneities in subsurface lithology have proven to be primary controlling factor governing GM (Forde et al., 2019; Geistlinger et al., 2006, 2009; Selker et al., 2007). The 12 m silty diamict with a dense matrixsupported texture present at the HHFRS (Chao et al., in preparation) provided a relatively impermeable barrier for the gas plume. Findings from the early part of the injection experiment suggest that the free phase synthetic natural gas became entrapped underneath the confining layer and spreading laterally (Cary, 2019) in search for preferential pathways, and or until the free phase gas plume had sufficient pressure to overcome capillary barriers in the diamict. Current regulatory practices surrounding GM in BC are based on the assumption that the majority of the fugitive gas emissions at the ground surface occur proximal to the well-head (BC Oil & Gas Commission, 2019; Lyman et al., 2017; Smith et al., 2019). The current visual, olfactory, and or auditory techniques employed by operators to identify GM are not always sufficient to detect surface emissions (BC Oil & Gas Commission, 2019). However, results from Chapter 3 demonstrated that elevated effluxes were measured and localized 12 m north-west and upgradient of the groundwater

flow direction, while no significant fluxes could be observed near the injection well. For the first six weeks of this controlled release experiment, none of the introduced injection gas had migrated through the confining layer and into the vadose zone or surface. Once the synthetic natural gas made it to the surface through a primary preferential pathway, CH<sub>4</sub> effluxes at the ground surface were fluctuating but generally increasing until one-week post injection. The discontinuous migration of fugitive CH<sub>4</sub> is attributed to heterogeneities along preferential pathways that require different pore-scale entry pressure. The strong upwards migration of gas in this region of the field site is also supported by soil gas concentration data presented in Chapter 4. The quick decrease of gas effluxes after cessation of gas injection was likely associated with the dissipation of pressure in the free phase gas plume, resulting in insufficient pressure to overcome capillary forces. Soil gas data collected post-injection also provided evidence for the existence of alternative preferential pathways. Long-term and survey efflux measurements were used to estimate the fraction of the gas lost to the atmosphere. Despite substantial uncertainties with these calculations, these calculations indicate that the majority of the injected gas remained in the subsurface.

The fate of GM in the vadose zone was characterized by stable-carbon and stable-hydrogen isotopes of CO<sub>2</sub>, CH<sub>4</sub>, as well as C<sub>2</sub> and C<sub>3</sub> hydrocarbons. Stable-carbon and stable-hydrogen isotopes of soil-gas have been used in previous studies to identify the source of FG emissions (Bernard et al., 1978; Cathles et al., 2012; Humez et al., 2016; Jackson, 2014; Jackson et al., 2013; Singh et al., 2017; Whiticar, 1999). In this thesis, the  $\delta^{13}$ C-CH<sub>4</sub>,  $\delta^{2}$ H-CH<sub>4</sub>, and He concentrations (He was used as a tracer in the injection gas) were able to prove that the gas detected at the surface and in the vadose zone was from the introduced injection gas. Additionally, the enrichment of the heavier isotopes ( $\delta^{13}$ C and  $\delta^{2}$ H) in CH<sub>4</sub>, C<sub>2</sub> and C<sub>3</sub>, provides evidence for microbially mediated hydrocarbon oxidation. This thesis also confirms the findings of Forde et al. (2019), whereby less

isotopic fractionation was observed during periods of high effluxes and more isotopic fractionation occurred during periods of lower effluxes. Therefore, stable-carbon and stable-hydrogen isotopic values can be indicative of oxidation reactions and subsurface migration rates, if the isotopic signature of the gas source is known.

To more accurately detect fugitive emissions at the surface a spatially extensive monitoring network is required because it is not possible to predict regions where preferential pathways to the surface would occur. In the experiment by Forde et al. (2019), despite it being a similar experiment in the same region, all major effluxes were within 5 m of the gas release point and the monitoring network used for that experiment would have been insufficient in capturing effluxes at the HHFRS. Although episodic effluxes were not substantial in this study, fugitive effluxes can vary significantly day-to-day (Cahill et al., 2017; Forde et al., 2019), suggesting that relatively highresolution temporal data is needed to capture all aspects of the effluxes. To meet these requirements, an integrated chamber set-up (long-term and survey) combined with an EC system would be the most effective to capture fugitive emissions at the surface. This approach was used at the HHFRS; however, the EC data could not be fully analyzed, and it is the integration of the EC and flux chamber data is beyond the scope of this thesis. Nevertheless, a qualitative comparison of EC flux data and long-term chamber flux data, shows that emissions were captured over the same time frame and emission trends varied in similar ways, as quantified by both measurement methods.

In addition to monitoring of surface effluxes, meteorological parameters such as wind speed, precipitation and barometric pressure may also influence GM and may affect monitoring campaigns. Although barometric pressure fluctuations had a significant impact on surface gas effluxes in the study by Forde et al. (2019), completed in the same region, the impact of barometric

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pressure fluctuations was insignificant in the present study, likely due to the shallow water table. However, it was found that meteorological parameters did influence CH<sub>4</sub> effluxes: diurnal windspeed variations resulted in more varied and overall lower effluxes at night, and precipitation resulted in temporary and short-lived decreased effluxes (Chapter 3). Other studies have suggested that these impacts could be more significant (Börjesson et al., 2007; Christophersen & Kjeldsen, 2001; Kim et al., 2012; Zhang & Yang, 2015). Therefore, meteorological parameters should be taken into account when planning GM monitoring campaigns. Lastly, while surface expressions of fugitive emissions are important to characterize, GM in the subsurface has the potential to impact groundwater quality and result in a potential explosion hazard and should be delineated if possible (Jackson et al., 2013; Vengosh et al., 2014; Vidic et al., 2013).

Chapter 4 illustrated that post injection significant concentrations of the injected gas were detected at 1.15 m bgs more than 25 m away from the primary preferential pathway where the highest effluxes were detected. Therefore, monitoring wells with depth discrete gas and water samples would be ideal to constrain and monitor the extent and migration of GM in the subsurface.

Fugitive emissions at the HHFRS were only detected at the surface due to the presence of an imperfection in the confining layer. This emphasizes the importance of a detailed understanding of the local geology. Regardless of whether this imperfection is an artifact of the installation of monitoring wells or present as a natural pre-existing pathway, this study shows that sites affected by GM with confining low permeability soils near the ground surface may produce highly localized gas emissions. The location of preferential pathways is difficult, if not impossible to predict. Without the imperfection in the surface cover, it is likely that the free phase gas plume would continue to migrate laterally under lower permeability layers until an alternative pathway was found or it would remain entirely in the subsurface without any surface expression. The EC CH<sub>4</sub> efflux data presented in this thesis is the main subject of a companion thesis and has not been fully processed at the time of writing. As a result, an integration of EC and chamber data could not be completed at this time. Therefore, a comparative estimate of fugitive emission to the atmosphere using both methods could not be provided.

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# Appendices

## Appendix A Temporary Survey Grid

A temporary survey grid was set up as a 14 m by 12 m grid around MW2 to attempt to locate

hot-spot regions and better select the new locations for six long-term chambers.



**Figure A.1:** Location of the temporary grid set-up to measure CH<sub>4</sub> and CO<sub>2</sub> effluxes around MW2. This survey measurement informed the placement of the long-term chambers.

## Appendix B Individual Long-term Chamber Efflux Results

This appendix contains all the CO<sub>2</sub> and CH<sub>4</sub> efflux data for each long-term chamber location. For all figured the detection limit for CH<sub>4</sub> is 0.01  $\mu$ mol  $m^{-2}s^{-1}$ . All fluxes below this threshold have been filtered out.

The chamber names are based on labelling in Figure 1 (below).



Figure B.1: Labelled long-term chambers and their relative locations on a site map.



**Figure B.2:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>) (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT1. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.3:** (A): CH<sub>4</sub> fluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>), measured by LT2. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.4:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT3. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.5:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT4. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.6:** (A): CH<sub>4</sub> fluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>), measured by LT5. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.7:** (A): CH<sub>4</sub> fluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>), measured by LT6. The blue and orange datapoints are fluxes measured during the night and day time respectively.


**Figure B.8:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT7. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.9:** (A): CH<sub>4</sub> fluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes ( $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>), measured by LT8. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.10:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT9. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.11:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT10. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.12:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT11. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.13:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT12. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.14:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT13. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.15:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT14. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.16:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT15. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.17:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT16. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.18:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT17. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.19:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT18. The blue and orange datapoints are fluxes measured during the night and day time respectively.



**Figure B.20:** (A): CH<sub>4</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), (B): CO<sub>2</sub> fluxes (µmol m<sup>-2</sup> s<sup>-1</sup>), measured by LT19. The blue and orange datapoints are fluxes measured during the night and day time respectively.

## Appendix C Background CO<sub>2</sub> and CH<sub>4</sub> Survey Measurements

This appendix contains all the CO<sub>2</sub> and CH<sub>4</sub> efflux surveys that were not included in the thesis. For the purposes of trend demonstration, the data was not filtered with the detection limit of  $0.01 \mu mol \ m^{-2} s^{-1}$ . However, the data has undergone quality control and appropriate filtering.



Figure C.1: (A): the CO<sub>2</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>, (B): the CH<sub>4</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> for June 1, 2018.



June 12, 2018

Figure C.2: (A): the CO<sub>2</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>, (B): the CH<sub>4</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> for June 12, 2018.





Figure C.3: (A): the CO<sub>2</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. (B): the CH<sub>4</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> for June 13, 2018.



Figure C.4: (A): the CO<sub>2</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. (B): the CH<sub>4</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> for June 26, 2018.





Figure C.5: (A): the CO<sub>2</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>. (B): the CH<sub>4</sub> effluxes in  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup> for June 28, 2018.

## Appendix D Soil Gas Composition Data

	Depth	_				Soil Gas	Location (based on				
Sample ID	(m bgs)	Date	Ar	<b>O</b> <sub>2</sub>	$N_2$	<b>CO</b> <sub>2</sub>	CH4	C2	С3	Well	gas release point)
11B1-LT3	0.45	2018-08-15	0.88	20.32	77.46	1.04	0.0002	BDL	BDL	SG1	12 m South
02R1-LT3	1.15	2018-06-09	0.91	19.99	78.28	0.88	0.0002	BDL	BDL	SG1	12 m South
05R1-LT3	1.15	2018-06-14	0.90	20.35	78.33	0.56	0.0002	BDL	BDL	SG1	12 m South
09R1-LT3	1.15	2018-07-27	0.87	19.07	79.08	0.65	0.0002	BDL	BDL	SG1	12 m South
11R1-LT3	1.15	2018-08-15	0.85	20.30	77.27	1.02	0.0002	BDL	BDL	SG1	12 m South
14B1-LT3	0.45	2019-06-26	0.89	20.38	77.67	0.37	0.0003	BDL	BDL	SG1	12 m South
14R1-LT3	1.15	2019-06-26	0.90	20.56	77.57	0.30	0.0003	BDL	BDL	SG1	12 m South
02B1-LT3	0.45	2018-06-09	0.86	19.37	78.20	1.39	BDL	BDL	BDL	SG1	12 m South
05B1-LT3	0.45	2018-06-14	0.90	19.63	78.14	1.52	BDL	BDL	BDL	SG1	12 m South
09B1-LT3	0.45	2018-07-27	0.94	16.20	80.45	2.02	BDL	BDL	BDL	SG1	12 m South
14B1-LT2	0.45	2019-06-26	0.92	17.97	78.78	1.63	0.0001	BDL	BDL	SG10	6 m East
05R1-LT2	1.15	2018-06-14	0.88	20.14	78.14	0.90	0.0002	BDL	BDL	SG10	6 m East
07R1-LT2	1.15	2018-06-27	0.89	18.42	79.18	1.34	0.0002	BDL	BDL	SG10	6 m East
14R1-LT2	1.15	2019-06-26	0.92	20.48	77.41	0.33	0.0003	BDL	BDL	SG10	6 m East
02B1-LT2	0.45	2018-06-09	0.88	19.84	77.83	1.39	BDL	BDL	BDL	SG10	6 m East
05B1-LT2	0.45	2018-06-14	0.90	19.97	77.85	1.32	BDL	BDL	BDL	SG10	6 m East
07B1-LT2	0.45	2018-06-27	0.92	17.87	79.76	1.42	BDL	BDL	BDL	SG10	6 m East
14B1-LT25	0.45	2019-06-26	0.93	18.76	78.10	1.52	0.0001	BDL	BDL	SG11	12 m East
14R1-LT25	1.15	2019-06-26	0.87	20.45	77.48	0.45	0.0002	BDL	BDL	SG11	12 m East
02B1-LT5	0.45	2018-06-09	0.92	16.94	79.57	2.51	BDL	BDL	BDL	SG11	12 m East
05B1-LT5	0.45	2018-06-14	0.89	17.35	79.24	2.70	BDL	BDL	BDL	SG11	12 m East
05R1-LT5	1.15	2018-06-14	0.93	16.64	80.60	1.91	BDL	BDL	BDL	SG11	12 m East

Table D.1: A full list of all samples, sample ID, depth, the soil gas port and % (v/v) for Ar, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub> and C<sub>3</sub>.

02B1-LT8	0.45	2018-06-09	0.88	18.71	78.67	1.69	BDL	BDL	BDL	SG12	26 m East
05B1-LT8	0.45	2018-06-14	0.88	18.85	78.32	1.85	BDL	BDL	BDL	SG12	26 m East
02R1-LT8	1.15	2018-06-09	0.93	18.12	79.65	1.24	BDL	BDL	BDL	SG12	26 m East
05R1-LT8	1.15	2018-06-14	0.91	18.13	79.47	1.40	BDL	BDL	BDL	SG12	26 m East
14R1-LT3'	1.15	2019-06-26	0.94	17.61	78.12	2.91	0.0001	BDL	BDL	SG15	5.2 m north-east
14B1-LT3'	0.45	2019-06-26	0.89	19.92	78.17	0.61	0.0011	0.0002	BDL	SG15	5.2 m north-east
11B1-LT3'	0.45	2018-08-15	0.89	20.52	77.92	0.59	0.0022	0.0001	0.0002	SG15	5.2 m north-east
10B1-LT3'	0.45	2018-08-08	0.90	20.50	78.16	0.51	0.0023	0.0003	0.0005	SG15	5.2 m north-east
12B1-LT3'	0.45	2018-08-24	0.95	20.58	77.84	0.49	0.0036	0.0004	0.0006	SG15	5.2 m north-east
12R1-LT3'	1.15	2018-08-24	0.94	19.95	77.47	1.66	0.0099	0.0005	0.0016	SG15	5.2 m north-east
13B1-LT3'	0.45	2018-09-13	0.91	20.13	78.26	0.53	0.0289	0.0012	0.0010	SG15	5.2 m north-east
11R1-LT3'	1.15	2018-08-15	0.87	18.79	77.57	2.55	0.0402	0.0022	0.0039	SG15	5.2 m north-east
13R1-LT3'	1.15	2018-09-13	0.92	19.58	78.05	1.08	0.0620	0.0022	0.0022	SG15	5.2 m north-east
10R1-LT3'	1.15	2018-08-08	0.87	18.00	77.64	3.29	0.1492	0.0086	0.0071	SG15	5.2 m north-east
14B1-LT5'	0.45	2019-06-26	0.90	19.85	78.26	0.45	0.0002	BDL	BDL	SG17	10 m north-east
14R1-LT5'	1.15	2019-06-26	0.90	17.20	78.89	2.50	0.0002	BDL	BDL	SG17	10 m north-east
AIR1LT5'		2018-08-24	0.88	21.00	77.98	0.05	0.0008	BDL	BDL	SG17	10 m north-east
10B1-LT5'	0.45	2018-08-08	0.86	20.55	77.80	0.26	0.1182	0.0090	0.0055	SG17	10 m north-east
12B1-LT5'	0.45	2018-08-24	0.88	20.74	77.75	0.39	0.2180	0.0164	0.0101	SG17	10 m north-east
10R1-LT5'	1.15	2018-08-08	0.90	20.32	77.74	0.50	0.4873	0.0337	0.0191	SG17	10 m north-east
13B1-LT5'	0.45	2018-09-13	0.89	20.04	77.92	0.35	0.5383	0.0336	0.0173	SG17	10 m north-east
11B1-LT5'	0.45	2018-08-15	0.90	20.11	77.15	0.94	0.6437	0.0496	0.0283	SG17	10 m north-east
13R1-LT5'	1.15	2018-09-13	0.88	19.30	77.82	0.79	1.0702	0.0612	0.0308	SG17	10 m north-east
12R1-LT5'	1.15	2018-08-24	0.90	19.84	76.41	1.08	1.4745	0.1091	0.0596	SG17	10 m north-east
11R1-LT5'	1.15	2018-08-15	0.86	18.82	75.87	1.60	2.4410	0.1687	0.0841	SG17	10 m north-east
14B1-LT6'	0.45	2019-06-26	0.90	18.06	79.46	0.99	0.0003	BDL	BDL	SG18	13 m north-east
14R1-LT6'	1.15	2019-06-26	0.89	18.68	78.61	1.17	0.0003	BDL	BDL	SG18	13 m north-east
AIR1LT6'		2018-08-24	0.85	20.85	77.95	0.07	0.0007	BDL	BDL	SG18	13 m north-east

13B1-LT6'	0.45	2018-09-13	0.94	17.03	77.66	0.77	3.3125	0.1701	0.0849	SG18	13 m north-east
13R1-LT6'	1.15	2018-09-13	0.86	16.46	76.78	1.12	4.1042	0.2498	0.1452	SG18	13 m north-east
12R1-LT6'	1.15	2018-08-24	0.81	19.07	73.61	0.79	5.0514	0.3793	0.2017	SG18	13 m north-east
12B1-LT6'	0.45	2018-08-24	0.79	18.45	71.24	0.86	7.6233	0.6223	0.3418	SG18	13 m north-east
11B1-LT6'	0.45	2018-08-15	0.69	15.18	63.97	2.02	15.9374	1.2623	0.7094	SG18	13 m north-east
10B1-LT6'	0.45	2018-08-08	0.75	13.85	59.97	2.03	21.3156	1.4737	0.7373	SG18	13 m north-east
11R1-LT6'	1.15	2018-08-15	0.57	8.68	48.85	3.20	34.7883	2.6623	1.4166	SG18	13 m north-east
14B1-LT1	0.45	2019-06-26	0.91	19.07	78.13	1.11	0.0001	BDL	BDL	SG2	6 m South
05R1-LT1	1.15	2018-06-14	0.86	20.14	78.16	0.66	0.0002	BDL	BDL	SG2	6 m South
11B1-LT1	0.45	2018-08-15	0.87	20.14	77.40	1.21	0.0003	BDL	BDL	SG2	6 m South
14R1-LT1	1.15	2019-06-26	0.91	20.39	77.48	0.44	0.0003	BDL	BDL	SG2	6 m South
09B1-LT1	0.45	2018-07-27	0.95	12.66	83.29	2.97	0.0004	BDL	BDL	SG2	6 m South
13R1-LT1	1.15	2018-09-13	0.92	19.88	78.29	0.68	0.0006	BDL	0.0001	SG2	6 m South
09R3-LT1	1.15	2018-07-27	0.89	19.28	79.10	0.61	0.0007	BDL	BDL	SG2	6 m South
12R1-LT1	1.15	2018-08-24	0.87	20.55	77.78	0.79	0.0012	0.0002	0.0002	SG2	6 m South
13B1-LT1	0.45	2018-09-13	0.90	19.11	78.83	0.98	0.0019	0.0001	0.0001	SG2	6 m South
12B1-LT1	0.45	2018-08-24	0.87	20.42	77.47	1.03	0.0056	0.0012	0.0012	SG2	6 m South
02B1-LT1	0.45	2018-06-09	0.87	18.99	78.75	1.64	BDL	BDL	BDL	SG2	6 m South
05B1-LT1	0.45	2018-06-14	0.93	19.29	78.12	1.80	BDL	BDL	BDL	SG2	6 m South
02R1-LT1	1.15	2018-06-09	0.87	19.14	78.54	1.41	BDL	BDL	BDL	SG2	6 m South
11R1-LT1	1.15	2018-08-15	0.88	19.74	76.73	2.35	BDL	BDL	BDL	SG2	6 m South
13B1-S3	0.45	2018-09-13	0.87	19.67	78.21	1.06	0.0003	BDL	BDL	SG22	North-east corner
02R1-S3	1.15	2018-06-09	0.88	20.68	78.26	0.15	0.0003	BDL	BDL	SG22	North-east corner
11R1-S3	1.15	2018-08-15	0.85	20.48	78.09	0.36	0.0003	BDL	BDL	SG22	North-east corner
05B1-S3	0.45	2018-06-14	0.88	19.25	77.65	2.09	0.0004	0.0001	0.0001	SG22	North-east corner
13R1-S3	1.15	2018-09-13	0.90	20.56	77.98	0.34	0.0004	BDL	BDL	SG22	North-east corner
05R1-S3	1.15	2018-06-14	0.89	20.60	78.23	0.38	0.0008	0.0001	BDL	SG22	North-east corner
11B1-S3	0.45	2018-08-15	0.90	19.73	77.00	2.15	BDL	BDL	BDL	SG22	North-east corner

13B1-S22	0.45	2018-09-13	0.87	18.90	78.75	1.27	0.0003	BDL	BDL	SG23	North-west corner
14B1-S22	0.45	2019-06-26	0.87	18.60	78.30	1.25	0.0003	BDL	BDL	SG23	North-west corner
02R1-S22	1.15	2018-06-09	0.86	20.75	78.15	0.15	0.0004	BDL	BDL	SG23	North-west corner
12B1-S22	0.45	2018-08-24	0.89	20.07	77.26	1.74	0.0007	0.0001	0.0001	SG23	North-west corner
13R1-S22	1.15	2018-09-13	0.84	20.28	78.34	0.53	0.0007	BDL	BDL	SG23	North-west corner
02B1-S22	0.45	2018-06-09	0.90	18.70	78.62	1.77	BDL	BDL	BDL	SG23	North-west corner
11B1-S22	0.45	2018-08-15	0.88	19.36	76.79	2.84	BDL	BDL	BDL	SG23	North-west corner
02B1-S17	1.15	2018-06-09	0.89	18.46	79.55	1.10	BDL	BDL	BDL	SG25	South-west corner
14B1-S11	0.45	2019-06-26	0.90	19.03	78.17	1.21	0.0001	BDL	BDL	SG26	25 m South
02R1-S11	1.15	2018-06-09	0.88	20.12	77.98	0.90	0.0002	BDL	BDL	SG26	25 m South
14R1-S11	1.15	2019-06-26	0.90	19.60	77.77	1.05	0.0002	BDL	BDL	SG26	25 m South
02B1-S11	0.45	2018-06-09	0.84	19.76	78.01	1.25	BDL	BDL	BDL	SG26	25 m South
14B1-S8	0.45	2019-06-26	0.88	17.95	78.69	1.69	0.0001	BDL	BDL	SG27	South-east corner
02R1-S8	1.15	2018-06-09	0.93	19.55	78.46	1.10	0.0003	BDL	BDL	SG27	South-east corner
14R1-S8	1.15	2019-06-26	0.90	20.19	77.66	0.57	0.0003	BDL	BDL	SG27	South-east corner
02B1-S8	0.45	2018-06-09	0.88	19.44	78.19	1.49	BDL	BDL	BDL	SG27	South-east corner
14R1-LT7	1.15	2019-06-26	0.89	20.44	77.42	0.41	0.0002	BDL	BDL	SG3	3 m South
14B1-LT7	0.45	2019-06-26	0.92	18.09	78.83	1.47	0.0003	0.0001	BDL	SG3	3 m South
05R1-LT7	1.15	2018-06-14	0.89	20.04	78.34	0.61	0.0003	BDL	BDL	SG3	3 m South
02B1-LT7	0.45	2018-06-09	0.95	18.97	78.41	1.80	BDL	BDL	BDL	SG3	3 m South
05B1-LT7	0.45	2018-06-14	0.88	19.25	78.01	1.99	BDL	BDL	BDL	SG3	3 m South
11B1-LT7	0.45	2018-08-15	0.89	19.70	76.76	2.31	BDL	BDL	BDL	SG3	3 m South
11B2-LT7	0.45	2018-08-15	0.92	19.68	76.89	2.39	BDL	BDL	BDL	SG3	3 m South
02R1-LT7	1.15	2018-06-09	0.88	18.16	79.19	1.69	BDL	BDL	BDL	SG3	3 m South
14B1-LT6	0.45	2019-06-26	0.90	17.58	79.20	1.84	0.0001	BDL	BDL	SG4	2 m South
02R1-LT6	1.15	2018-06-09	0.87	19.31	78.60	1.29	0.0002	BDL	BDL	SG4	2 m South
07R1-LT6	1.15	2018-06-27	0.89	19.46	78.92	0.74	0.0002	BDL	BDL	SG4	2 m South
11R1-LT6	1.15	2018-08-15	0.88	20.36	77.62	0.74	0.0002	BDL	BDL	SG4	2 m South

13B1-LT6	0.45	2018-09-13	0.90	18.70	78.95	1.28	0.0003	BDL	0.0001	SG4	2 m South
05R1-LT6	1.15	2018-06-14	0.88	19.99	78.39	0.70	0.0003	BDL	BDL	SG4	2 m South
14R1-LT6	1.15	2019-06-26	0.91	20.48	77.71	0.39	0.0003	BDL	BDL	SG4	2 m South
13R1-LT6	1.15	2018-09-13	0.89	20.20	78.23	0.56	0.0004	BDL	BDL	SG4	2 m South
12R1-LT6	1.15	2018-08-24	0.87	20.48	77.56	0.83	0.0006	0.0001	0.0001	SG4	2 m South
12B1-LT6	0.45	2018-08-24	0.91	20.21	77.43	1.28	0.0013	0.0002	0.0001	SG4	2 m South
02B1-LT6	0.45	2018-06-09	0.90	18.55	78.33	2.30	BDL	BDL	BDL	SG4	2 m South
05B1-LT6	0.45	2018-06-14	0.88	18.82	78.10	2.44	BDL	BDL	BDL	SG4	2 m South
07B1-LT6	0.45	2018-06-27	0.91	15.70	81.16	2.12	BDL	BDL	BDL	SG4	2 m South
11B1-LT6	0.45	2018-08-15	0.88	19.41	76.57	2.97	BDL	BDL	BDL	SG4	2 m South
14B1-LT9	0.45	2019-06-26	0.92	17.40	79.20	1.97	0.0001	BDL	BDL	SG5	1 m South
02R1-LT9	1.15	2018-06-09	0.92	19.78	78.42	0.98	0.0002	BDL	BDL	SG5	1 m South
05R1-LT9	1.15	2018-06-14	0.89	19.95	78.58	0.76	0.0002	BDL	BDL	SG5	1 m South
07R1-LT9	1.15	2018-06-27	0.88	20.16	78.56	0.41	0.0002	BDL	BDL	SG5	1 m South
11R1-LT9	1.15	2018-08-15	0.93	20.53	77.73	0.38	0.0003	BDL	BDL	SG5	1 m South
14R1-LT9	1.15	2019-06-26	0.87	20.31	77.67	0.52	0.0003	BDL	BDL	SG5	1 m South
13B1-LT9	0.45	2018-09-13	0.93	17.85	79.80	1.48	0.0004	BDL	BDL	SG5	1 m South
13R1-LT9	1.15	2018-09-13	0.88	19.80	78.75	0.69	0.0008	BDL	BDL	SG5	1 m South
12B1-LT9	0.45	2018-08-24	0.90	20.16	77.53	1.36	0.0009	0.0002	0.0002	SG5	1 m South
12R1-LT9	1.15	2018-08-24	0.89	20.63	77.76	0.65	0.0061	0.0006	0.0004	SG5	1 m South
02B1-LT9	0.45	2018-06-09	0.87	19.09	78.11	1.91	BDL	BDL	BDL	SG5	1 m South
05B1-LT9	0.45	2018-06-14	0.88	19.45	77.94	1.88	BDL	BDL	BDL	SG5	1 m South
07B1-LT9	0.45	2018-06-27	0.93	15.74	81.10	2.14	BDL	BDL	BDL	SG5	1 m South
10B1-LT9	0.45	2018-08-08	0.90	18.67	77.02	3.69	BDL	0.0002	0.0001	SG5	1 m South
11B1-LT9	0.45	2018-08-15	0.84	19.63	76.90	2.23	BDL	BDL	BDL	SG5	1 m South
14R1-LT11	1.15	2019-06-26	0.91	18.70	78.57	0.97	0.0001	BDL	BDL	SG7	1 m East
05R1-LT11	1.15	2018-06-14	0.85	19.74	78.39	0.98	0.0002	BDL	BDL	SG7	1 m East
07R1-LT11	1.15	2018-06-27	0.83	20.46	78.41	0.22	0.0003	BDL	BDL	SG7	1 m East

02B1-LT12	0.45	2018-06-09	0.86	18.79	78.84	1.64	BDL	BDL	BDL	SG7	1 m East
05B1-LT11	0.45	2018-06-14	0.86	19.31	78.35	1.47	BDL	BDL	BDL	SG7	1 m East
07B1-LT11	0.45	2018-06-27	0.89	19.79	78.71	0.53	BDL	BDL	BDL	SG7	1 m East
14B1-LT11	0.45	2019-06-26	0.96	17.16	79.57	1.47	BDL	BDL	BDL	SG7	1 m East
02R1-LT12	1.15	2018-06-09	0.91	18.36	79.55	1.49	BDL	BDL	BDL	SG7	1 m East
14B1-LT14	0.45	2019-06-26	0.93	18.38	78.73	1.01	0.0002	BDL	BDL	SG8	2 m East
05R1-LT14	1.15	2018-06-14	0.90	19.30	79.11	0.92	0.0002	BDL	BDL	SG8	2 m East
14R1-LT14	1.15	2019-06-26	0.90	19.49	77.93	0.89	0.0002	BDL	BDL	SG8	2 m East
07R1-LT14	1.15	2018-06-27	0.86	20.35	78.38	0.36	0.0003	BDL	BDL	SG8	2 m East
11R1-LT14	1.15	2018-08-15	0.89	19.29	78.28	1.15	0.0003	BDL	BDL	SG8	2 m East
13R1-LT14	1.15	2018-09-13	0.91	19.26	78.84	0.80	0.0004	BDL	BDL	SG8	2 m East
13B1-LT14	0.45	2018-09-13	0.95	13.49	83.58	1.75	0.0009	BDL	BDL	SG8	2 m East
02B1-LT14	0.45	2018-06-09	0.90	17.39	79.00	2.83	BDL	BDL	BDL	SG8	2 m East
05B1-LT14	0.45	2018-06-14	0.86	17.64	78.78	2.86	BDL	BDL	BDL	SG8	2 m East
07B1-LT14	0.45	2018-06-27	0.91	14.49	81.61	2.83	BDL	BDL	BDL	SG8	2 m East
11B1-LT14	0.45	2018-08-15	0.86	18.12	76.30	4.86	BDL	BDL	BDL	SG8	2 m East
14B1-LT10	0.45	2019-06-26	0.93	17.41	79.04	1.76	0.0001	BDL	BDL	SG9	3 m East
14R1-LT10	1.15	2019-06-26	0.91	17.58	78.61	2.14	0.0001	BDL	BDL	SG9	3 m East
05B1-LT10	0.45	2018-06-14	0.89	20.02	77.95	1.09	0.0002	BDL	BDL	SG9	3 m East
02B2-LT10	0.45	2018-06-09	0.88	19.38	78.05	1.62	BDL	BDL	BDL	SG9	3 m East
05R1-LT10	1.15	2018-06-14	0.87	19.05	78.01	2.01	BDL	BDL	BDL	SG9	3 m East

BDL = Below the Detection Limit





Figure E.1: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG1.



Figure E.2: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG2.



Figure E.3: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG3.



Figure E.4: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG4.



Figure E.5: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG5.



Figure E.6: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG7.



Figure E.7: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG8.



Figure E.8: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG9.



Figure E.9: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG10.



Figure E.10: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG11.



Figure E.11: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG15.



Figure E.12: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG17.



Figure E.13: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG18.



Figure E.14: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG22.



Figure E.15: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG23.



Figure E.16: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG25.



Figure E.17: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG26.



Figure E.18: (A): % (v/v) for CH<sub>4</sub>, (B): % (v/v) for C<sub>2</sub>H<sub>6</sub>, (C): % (v/v) for CO<sub>2</sub>, and (D): % (v/v) for N<sub>2</sub>, for SG27.