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### Key Points:

- Fugitive gas migrated to the ground surface despite a deep vadose zone with low-permeability silts and clays
- A preferential pathway and intervals of decreased barometric pressure resulted in a hotspot with high episodic methane effluxes
- Low-permeability sediments and intervals of increased barometric pressure favored lateral gas migration and progressive methane oxidation

### Supporting Information:

Supporting Information may be found in the online version of this article.

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## Fugitive Gas Migration in the Vadose Zone at an Experimental Field Site in the Montney Shale Gas Region

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**Abstract** Fugitive gas migration (GM) from compromised oil and gas wells remains a global concern. To understand environmental impacts from GM there is a need to characterize the transport and fate of fugitive gas in the vadose zone. We simulated subsurface wellbore leakage by injecting natural gas into thick unsaturated glacio-lacustrine deposits in a region of petroleum development in Western Canada. Methane and carbon dioxide effluxes were monitored and soil-gas samples were collected for molecular and stable carbon isotope analyses. A conceptual model was developed to demonstrate the physical and biogeochemical processes that control the spatial-temporal variability of GM. Methane oxidation partially attenuated natural gas; however, gas transport and fate were strongly influenced by variations in grain-size distribution and barometric pressure, resulting in episodic effluxes and lateral gas transport. To accurately detect, quantify and assess GM at oil and gas sites, adequate site characterization and continuous, spatially dense monitoring are necessary.

**Plain Language Summary** Natural gas leaking from imperfectly sealed oil and gas wells can lead to explosive conditions in soil gas and methane emissions to the atmosphere. To understand the impacts and improve monitoring practices of fugitive gas migration, there is a need to characterize processes that control gas transport and fate in the unsaturated zone. We simulated subsurface wellbore leakage by injecting natural gas into thick unsaturated deposits in a region of petroleum development in Western Canada. The response was monitored by measuring methane and carbon dioxide concentrations and emissions on the ground surface and in soil gas in the unsaturated zone. Our results show that numerous compounding processes influence methane concentrations in the unsaturated zone and emissions to the atmosphere. While microbially mediated reactions consume methane in the unsaturated zone, variations in soil grain sizes and changes in barometric pressure strongly influence gas transport, which can lead to high episodic emissions in unpredictable locations. To accurately detect, quantify and assess fugitive gas migration at oil and gas well sites, adequate site characterization and continuous, spatially dense monitoring are necessary.

## 1. Introduction

Natural gas (primarily methane, CH<sub>4</sub>) can leak from imperfectly sealed oil and gas wells and subsequently migrate through the subsurface toward the atmosphere (Ingraffea et al., 2014; Kiran et al., 2017; Sherwood et al., 2016). Fugitive gas migration (GM) within the subsurface can cause aquifer contamination (McMahon et al., 2018; Soeder, 2018) and explosive conditions in soil gas (Engelder & Zevenbergen, 2018; Kelly et al., 1985; Williams & Aitkenhead, 1991). Fugitive gas that reaches the ground surface and enters the atmosphere thereby contributes to greenhouse gas (GHG) emissions (Bachu, 2017; Lan et al., 2015; Lebel et al., 2020; Zavala-Araiza et al., 2015). To identify the occurrence of GM, it is often a regulatory standard to collect shallow soil-gas samples and/or measure efflux at the ground surface in close proximity to the oil and gas wellhead during a one-time monitoring event (Alberta Energy Regulator, 2021; BC Oil and Gas Commission, 2018; Fleming et al., 2021; Forde, Mayer, & Hunkeler, 2018).

Recent studies have revealed that the spatial and temporal patterns of fugitive gas effluxes at the ground surface can be strongly irregular, which can hinder detection and quantification of GM associated with oil and gas wells (Fleming et al., 2021; Forde, Mayer, & Hunkeler, 2018; Lyman et al., 2017, 2020; Schout et al., 2019). Spatio-temporal variations in gas effluxes have been attributed to a range of environmental factors including changes

in barometric pressure (Fleming et al., 2021; Forde et al., 2019; Lyman et al., 2020), wind speed (Fleming et al., 2021; Ulrich et al., 2019), and differences between atmospheric and soil temperatures and associated temperature fluctuations (Fleming et al., 2021; Xu et al., 2014). As a result, measurements of emissions at the ground surface only provide a partial view of GM. In many cases, fugitive gas is released into the saturated zone from where it can migrate vertically and laterally in the dissolved phase or as a free gas phase. The extent of GM is influenced by a multitude of factors including aquifer heterogeneity, presence of low permeability layers, natural gas leakage rates and depth of release, and the attenuation capacity for natural gas in the aquifer (Molofsky et al., 2021), including subsurface microbial CH<sub>4</sub> oxidation (Lyman et al., 2017, 2020; Schout et al., 2019). While CH<sub>4</sub> dissolution can result in a significant amount of gas retention in an aquifer (Chao et al., 2021; Schout et al., 2020), degassing and free phase GM can allow gas to escape into the vadose zone and subsequently into the atmosphere (Cahill et al., 2017; Van De Ven & Mumford, 2020). In some cases, vadose zone GM has been identified with no or limited CH<sub>4</sub> emissions detected at the ground surface (Lyman et al., 2017; McMahon et al., 2018; Schout et al., 2019), indicating a high potential for attenuation. In summary, CH<sub>4</sub> effluxes at the ground surface are controlled by a multitude of complex and compounding, poorly understood subsurface gas-transport phenomena and biogeochemical processes. The physical and biogeochemical processes that control the transport and fate of fugitive gas in the saturated and vadose zones need to be better characterized to evaluate environmental impacts from fugitive gas and to improve current monitoring and detection strategies. In this study, we focus on processes occurring in the vadose zone in response to either a direct release of fugitive gas into the vadose zone, or gas release from the saturated zone into the vadose zone.

In the vadose zone, the presence of oxygen (O<sub>2</sub>) can allow CH<sub>4</sub> to be attenuated through aerobic microbial CH<sub>4</sub> oxidation driven by methanotrophs to produce carbon dioxide (CO<sub>2</sub>) (Bogner et al., 1997; Börjesson et al., 2001; Stein & Hettiaratchi, 2001; M. J. Whiticar & Faber, 1986). Attenuation of CH<sub>4</sub> through microbial oxidation has been well documented in numerous settings, such as in landfill studies (Bogner et al., 1997; Börjesson et al., 2001; Christophersen et al., 2000) and at sites with petroleum hydrocarbon contamination (Landmeyer et al., 1996; Sihota & Mayer, 2012; Van De Ven et al., 2021). However, an understanding of the extent to which CH<sub>4</sub> from GM can be attenuated in the vadose zone remains limited, particularly at sites where complex gas transport processes occur in addition to biogeochemical attenuation processes. Some studies have hypothesized that a lack of fugitive CH<sub>4</sub> effluxes could be due to subsurface CH<sub>4</sub> oxidation (Lyman et al., 2017; McMahon et al., 2018), while other studies have observed evidence for both CH<sub>4</sub> oxidation and fugitive CH<sub>4</sub> effluxes (Forde, Mayer, Cahill, et al., 2018). There is a need to better understand the interaction between physical and biogeochemical processes in the vadose zone, and how they influence CH<sub>4</sub> emissions to the atmosphere.

Changes in barometric pressure affect gas transport in the vadose zone by creating pressure gradients between the atmosphere and subsurface (Massmann & Farrier, 1992). Periods of increasing barometric pressure inhibit upward migration of soil gas and reduce effluxes to the atmosphere, while periods of decreasing barometric pressure enhance advective transport of soil gas to the ground surface (Auer et al., 1996; Massmann & Farrier, 1992). The effects of barometric pressure changes on gas transport are more pronounced in a deeper vadose zone (Massmann & Farrier, 1992). This phenomena, “barometric pumping”, has been observed in numerous global settings including landfills (Czepiel et al., 2003; Gebert & Groengroeft, 2006; Xu et al., 2014) and at contaminated sites (Choi et al., 2002). In some instances, fugitive CH<sub>4</sub> effluxes at oil and gas well pads have been moderately correlated with barometric-pressure changes, however, at these sites the responses were likely dampened due to a thin vadose zone (Fleming et al., 2021; Lyman et al., 2020). Forde et al. (2019) demonstrated during an experimental natural-gas leak in a deep vadose zone, that the frequency and amplitude of barometric-pressure changes can directly control the magnitude and spatiotemporal distribution of CH<sub>4</sub> effluxes from the soil surface to the atmosphere (Forde et al., 2019).

Here, we present new data to build on the initial interpretations made by Forde et al. (2019) to more completely characterize the transport and fate of fugitive gas from the vadose zone to the ground surface and atmosphere. The additional data we present are from CH<sub>4</sub> and CO<sub>2</sub> efflux monitoring using long-term and survey chambers, and an extensive array of soil gas samples collected from various depths for molecular and stable-carbon isotope analyses. With this data, we provide new interpretations and develop a conceptual model that explains the physical and biogeochemical processes in the vadose zone controlling spatial-temporal variability of CH<sub>4</sub> effluxes. Our results have direct implications to inform more comprehensive monitoring strategies for the detection and quantification of GM from leaking oil and gas wells.

## 2. Materials and Methods

The field site is located in the region of the Montney resource play, Northeastern British Columbia, Canada, which has experienced extensive oil and gas development for conventional and unconventional hydrocarbon resources since the 1950's. The lithology of the 60-m deep vadose zone at our experimental field site is composed of a 10 m thick layer of distal glacio-lacustrine silts and clays (comprised of approximately 5 m of bedded silts and clays transitioning into silt with rare pebbles) underlain by proximal glacio-lacustrine silts and sands (Figure S1 in Supporting Information S1). A pressure transducer (vanEssen Instruments Baro-Diver) was installed at the field site to continuously measure barometric pressure and temperature. Simulated natural gas, with a composition similar to natural gas produced in the region (93.8% CH<sub>4</sub>, 1.8% C<sub>2</sub>H<sub>6</sub>, 0.2% C<sub>3</sub>H<sub>8</sub>, ~0.01% C<sub>4+</sub>, 3.0% N<sub>2</sub>, 0.3% CO<sub>2</sub>, 0.9% O<sub>2</sub>), was used to mimic leakage from an oil and gas well and to understand the physical and biogeochemical processes in response to natural gas intrusion in the vadose zone. Gas was injected for 5 days (7 m<sup>3</sup> d<sup>-1</sup>) 12 m below ground surface (bgs) (Text S1 in Supporting Information S1).

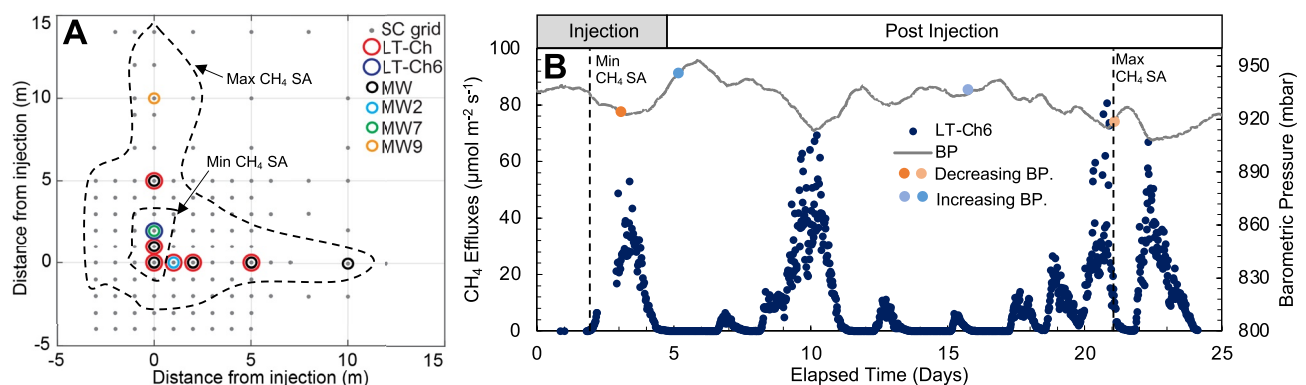
Soil-gas multilevel wells (MWs) were installed at nine locations across the site (Figure 1 and Table S1 in Supporting Information S1). Multilevel sampling ports were spaced in 1 m intervals from 1 to 12 m bgs. Soil-gas samples were analyzed for gas composition (CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and Ar) and stable-carbon isotope ratios (<sup>13</sup>C/<sup>12</sup>C) of CH<sub>4</sub> and CO<sub>2</sub> in the Isotope Science Laboratory at the University of Calgary (Alberta, Canada) (Text S1 in Supporting Information S1).

Across the site and co-located with multi-level soil-gas wells, seven long-term dynamic closed chambers (LT-Chs) (LI-8100-104, LI-COR Inc.) connected to a multiplexer (LI-COR LI-8150, LI-COR Inc.) and gas analyzers (LI-8100, LI-COR Inc., and UGGA, Los Gatos Research Inc.) were used to measure CH<sub>4</sub> and CO<sub>2</sub> effluxes (Figure 1 and Table S1 in Supporting Information S1). A survey chamber (SC) (LI-8100-103, LI-COR Inc.) connected to gas analyzers was used to measure effluxes across the site over 4–6 hr at up to 123 locations covering approximately 70 m<sup>2</sup> up to 15 m from the injection location (Figure 1). Details on the simulated natural gas injection, soil gas sampling, and soil efflux measurements are described in Text S1 in Supporting Information S1.

## 3. Results and Discussion

### 3.1. Methane Effluxes in Response to Changes in Barometric Pressure

Methane effluxes were first observed 2 days after the natural-gas injection began. The highest effluxes consistently occurred at LT-Ch6, 2 m from the injection location (Figures 1, S2, and Table S1 in Supporting Information S1). However, despite continuous gas release, effluxes declined from Day 3 to Day 5 (Figures 1 and S3 in Supporting Information S1). Total efflux rates and the surface area (SA) with observable effluxes fluctuated throughout the experiment. The SA was the smallest on Day 2 and the largest on Day 21 (Figure 1a). As discussed by Forde et al. (2019), there was a direct correlation between the rise and fall in barometric pressure and the decrease and



**Figure 1.** (a) Monitoring network including survey chamber (SC) grid, long-term chamber (LT-Ch) and monitoring well (MW) locations. LT-Ch6, marked by a blue circle, is where the highest CH<sub>4</sub> effluxes were measured. The minimum and maximum surface area (SA) of CH<sub>4</sub> efflux as measured by SC are shown with a black dashed line and were taken on Day 2 and Day 21, respectively. MW2, MW7, and MW9 for which soil-gas data are shown in Figure 2, are marked with blue, green, and yellow symbols, respectively. (b) CH<sub>4</sub> effluxes from LT-Ch6 plotted with barometric pressure over the duration of the experiment. Vertical dashed black lines indicate when the minimum and maximum SA of efflux were measured by SC. Soil-gas sampling events (see Figure 2) are indicated by the circles for decreasing (orange) and increasing (blue) barometric-pressure intervals.

increase in CH<sub>4</sub> effluxes, respectively, at all seven LT-Chs (Forde et al., 2019). A comprehensive understanding of the spatial and temporal CH<sub>4</sub> efflux patterns can be explained by the lithology of the site, barometric-pressure fluctuations, preferential-flow channels, and attenuation processes, as further explained below.

### 3.2. Subsurface Fugitive Gas Migration Processes in a Deep Vadose Zone

#### 3.2.1. Lithology

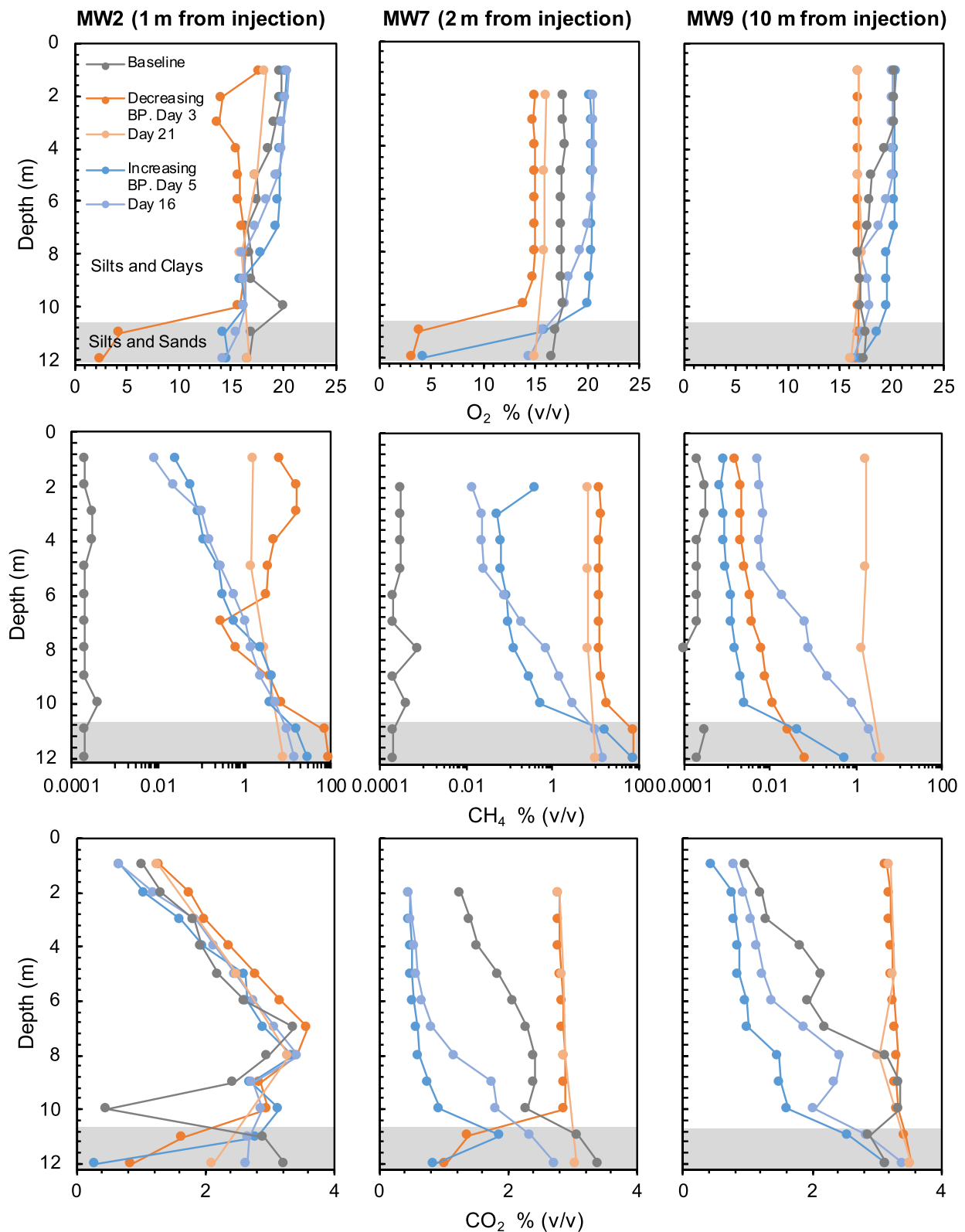
From approximately 12–11 m bgs, the vadose zone is comprised of proximal glacio-lacustrine silts and sands. Above 11 m there is a 10 m thick layer of low permeability distal glacio-lacustrine silts and clays (Figures S1 and S4 in Supporting Information S1). Methane was detected above baseline concentrations (non-detect to 0.0007% v/v; Table S2 in Supporting Information S1) at six of the MWs (up to 10 m from the injection location) that were sampled immediately after injecting natural gas. Elevated CH<sub>4</sub> coupled with depleted O<sub>2</sub>, N<sub>2</sub> and Ar concentrations were observed at the injection depth (12 m bgs) up to 11 m bgs, indicating soil gas displacement from gas injection (Figures 2 and S5 in Supporting Information S1). The persistence of elevated CH<sub>4</sub> concentrations also suggests that the low-permeability silts and clays at 10 m bgs acted as a barrier to limit vertical gas transport and thereby trapped natural gas at the injection depth. As a result, lateral GM was favored, which led to a rise in CH<sub>4</sub> gas concentrations and effluxes away from the injection location over time. This is seen by elevated CH<sub>4</sub> soil gas concentrations at MW9 on Day 16 and Day 21, as well as the greatest SA of CH<sub>4</sub> effluxes on Day 21 (Figures 1, 2, and S3 in Supporting Information S1). Fugitive gas effluxes detected at the ground surface 15 m from the injection location indicates that the injected gas may have migrated beyond our subsurface monitoring network. The effect of low-permeability sedimentary layers driving lateral gas transport has been observed in other studies with a deep vadose zone (Christophersen & Kjeldsen, 2001; Green et al., 2015). Despite knowledge of enhanced lateral GM under low-permeability sediments, monitoring for GM at oil and gas sites remains commonly limited to a confined area around the wellhead, in which case emissions could remain undetected or be underestimated.

#### 3.2.2. Barometric Pressure

The effect of barometric pumping on soil gas transport was most evident at MW7, 2 m from the injection location and co-located with LT-Ch6. Advection - dominated transport is indicated by a lack of vertical gradients in soil gas concentrations for CO<sub>2</sub>, CH<sub>4</sub>, and O<sub>2</sub> under intervals of decreasing barometric pressure, which resulted in elevated CO<sub>2</sub> and CH<sub>4</sub> with depleted O<sub>2</sub> through the vadose-zone profile (Figure 2). Although the fine-grained sedimentary layer limited vertical GM, at MW7 decreases in barometric pressure resulted in advective GM with vertical bulk movement of gas through the low-permeability sediments. This corresponded with a rise in CH<sub>4</sub> and CO<sub>2</sub> soil gas concentrations at MW7 and effluxes at the co-located LT-Ch6 (Figures 1 and 2). Increases in barometric pressure led to an ingress and mixing of atmospheric gas in the vadose zone, as seen by the O<sub>2</sub> elevated above baseline concentrations and decline in CH<sub>4</sub> and CO<sub>2</sub> concentrations and effluxes (Figures 1, 2, and S6 in Supporting Information S1).

At MW2, 1 m from the injection location and co-located with LT-Ch2, soil-gas concentrations demonstrate a response to changes in barometric pressure with slight variations with depth. For example, although barometric pressure was decreasing on Day 3, CH<sub>4</sub> concentrations at 7 and 8 m bgs were lower than under intervals of increasing barometric pressure (Figure 2). The lower CH<sub>4</sub> concentrations observed at this depth and time were coupled with an increase in CO<sub>2</sub> concentrations, which suggests enhanced microbial CH<sub>4</sub> oxidation. In general, however, CO<sub>2</sub> concentrations at MW2 decreased toward the ground surface, following baseline concentrations and agreeing with the lower CO<sub>2</sub> effluxes measured at LT-Ch2 (Figures 2 and S6 in Supporting Information S1). The vertical gradients in soil-gas concentrations at MW2 indicate that gas transport was more diffusive compared to the advective GM through a preferential pathway that was observed at MW7 (discussed below). The lack of enrichment in N<sub>2</sub> and Ar at MW2 and MW7 emphasizes that gas transport and mixing in the vadose zone were fast processes influenced by various factors including changes in barometric pressure (Figure S5 in Supporting Information S1).

At MW9, 10 m from the injection location but not co-located with a LT-Ch, soil-gas concentrations were also influenced by changes in barometric pressure, with the exception of higher CH<sub>4</sub> concentrations on Day 16 (increasing barometric pressure) compared to Day 3 (decreasing barometric pressure). The higher CH<sub>4</sub> concentration at



**Figure 2.** Gas concentration profiles for  $O_2$ ,  $CH_4$ , and  $CO_2$  measured before injection (gray) and during intervals of decreasing (orange, Day 3 and Day 21) and increasing (blue, Day 5 and Day 16) barometric pressure at MW2, MW7 and MW9 (see Figure 1). Although similar trends were observed at the other five MWs, these three wells were selected to provide a spatial representation of soil gas data across the site. The gray shaded region indicates the higher permeability sediments of silts and sands in comparison to the overlying lower permeability sediments of silts and clays.



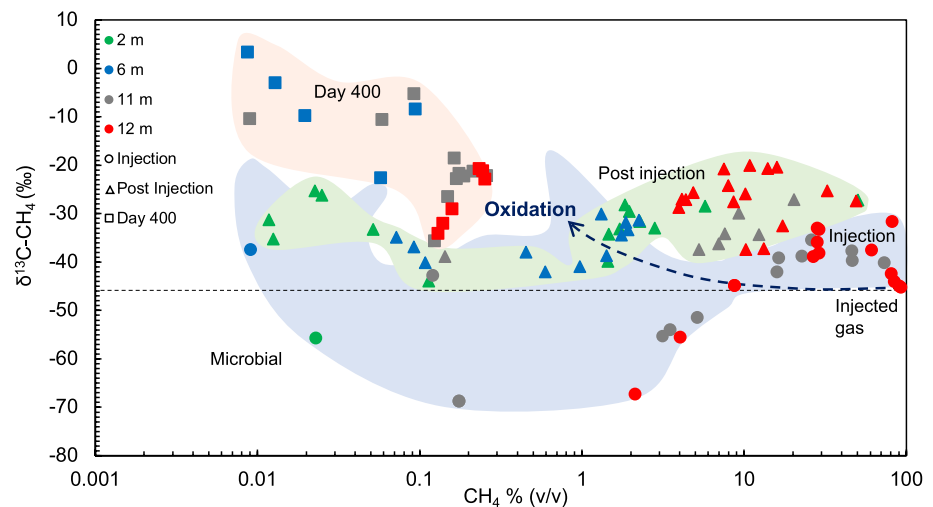
a later time period demonstrates the compounding influences of lithology and barometric pressure on gas transport. The low-permeability sediment barrier directed GM away from the injection site, a process which was enhanced during increasing barometric pressure intervals. During a period of decreasing barometric pressure, gas from 12 m bgs was drawn toward the ground surface, resulting in higher CH<sub>4</sub> soil-gas concentrations and widely distributed effluxes across the site (e.g., MW9, Figure 2, and effluxes shown in Figure S3 in Supporting Information S1). In studies on landfill GM, similar observations were made where soil-gas concentrations rapidly changed in response to barometric pressure changes (Christophersen & Kjeldsen, 2001; Gebert et al., 2011; Kjeldsen & Fischer, 1995).

### 3.2.3. Preferential Pathways

Preferential pathways can result in “hot spots” where CH<sub>4</sub> effluxes are much higher than other locations (Delahaye & Alonso Pérez de Agreda, 2002; Forde, Mayer, Cahill, et al., 2018; Tomlinson et al., 2003). The effect of barometric pumping through preferential pathways has been examined in the context of “breathing wells,” whereby a well installed in the vadose zone can provide a conduit for atmospheric interactions with the subsurface (Levintal et al., 2020; Neeper, 2003; You et al., 2011). The lack of vertical gradients in the soil-gas concentration profiles at MW7 coupled with the highest CH<sub>4</sub> effluxes at LT-Ch6 indicate the presence of a preferential pathway in this area (Figures 1 and 2). To understand how changes in barometric pressure can influence gas transport through such a preferential pathway, we estimated the volume and rate of gas that could be released through a geologic “conduit” under intervals of increasing and decreasing barometric pressure (Text S1 and Table S3 in Supporting Information S1). We assumed the system to be a 50 m<sup>3</sup> reservoir and changed the volume of the conduit between 1 and 0.01 m<sup>3</sup>. We hypothesized that gas was stored at the injection depth (12 m bgs), and that the conduit allowed barometric pressure changes to penetrate into the vadose zone. Using the total system volume and the magnitude and duration of a select interval of changing barometric pressure, we calculated the volume of gas released and the pore volume displaced through the conduit over the duration of the pressure change (Text S1 and Table S3 in Supporting Information S1). Under intervals of decreasing barometric pressure, with a small conduit volume (e.g., 0.01 m<sup>3</sup>) gas was released through the pathway at high velocities over a short duration (e.g., less than 1 hr). For example, from Day 1 to Day 3, a 16 mbar decrease in barometric pressure resulted in an estimated 0.87 m<sup>3</sup> of gas released at a velocity of 347 m d<sup>-1</sup> through a 0.01 m<sup>3</sup> conduit. In contrast, a 23 mbar increase in barometric pressure from Day 3 to Day 5, resulted in a downward velocity of 487 m d<sup>-1</sup> (i.e., no CH<sub>4</sub> released to the atmosphere). The results agree with similar studies, however, in different contexts not related to fugitive gas from leaking oil and gas wells, demonstrating that a conduit can enhance the effect of barometric-pressure changes on gas transport (Gebert et al., 2011; Levintal et al., 2020; Neeper, 2003; You et al., 2011). Although there may be multiple conduits at our field site, the soil-gas and efflux data from MW7 and LT-Ch6 indicate a key preferential pathway through the low-permeability sediments was present in this area, which allowed for barometric-pressure changes to lead to rapid gas release out of the reservoir and, for atmospheric gas to infiltrate the vadose zone. At the other six LT-Chs, a more subdued response to changes in barometric pressure was observed through lower magnitude CH<sub>4</sub> effluxes and no response in CO<sub>2</sub> effluxes (Figures S2 and S6 in Supporting Information S1). The lack of response in CO<sub>2</sub> effluxes, along with the limited change in CH<sub>4</sub> soil-gas concentrations, suggests that these areas were governed by more diffuse gas transport compared to the preferential GM around MW7/LT-Ch6. Vadose-zone gas data from other MWs also indicate that lower CH<sub>4</sub> effluxes can be attributed to suppression of vertical GM by lithological barriers (Figure 2).

### 3.2.4. Natural-Gas Attenuation

Stable carbon isotope ratios in hydrocarbon gases were only measured for CH<sub>4</sub>, as it was the major constituent of the simulated injected natural gas (93.8%), however, oxidation may have occurred for other hydrocarbons present at lower concentrations in the injected gas (1.8% C<sub>2</sub>H<sub>6</sub>, 0.2% C<sub>3</sub>H<sub>8</sub>, and ~0.01% C<sub>4</sub>+). The stable carbon isotope ratio of CH<sub>4</sub> (expressed as δ<sup>13</sup>C-CH<sub>4</sub>) in the injected natural gas was -45‰. Baseline CH<sub>4</sub> concentrations were <0.0007% v/v, below that needed to determine δ<sup>13</sup>C-CH<sub>4</sub> values. Over the period of natural gas injection, only two samples, collected on Day 2 and 3 from 12 m bgs, showed high CH<sub>4</sub> concentrations (>90% v/v) with a δ<sup>13</sup>C-CH<sub>4</sub> value identical to that of the injected gas (-45‰, Figure 3). The majority (i.e., 90%, n = 104) of samples collected for isotope analyses were characterized by <sup>13</sup>C-enriched CH<sub>4</sub> with δ<sup>13</sup>C-CH<sub>4</sub> values markedly higher than -45‰ and CH<sub>4</sub> concentrations less than in the injected gas. The highest δ<sup>13</sup>C-CH<sub>4</sub> value of +3‰ was observed on Day 400 in samples with CH<sub>4</sub> concentrations of up to 0.25% v/v (Figure 3). Microbial CH<sub>4</sub> oxidation results in preferential consumption of the light isotope, <sup>12</sup>C-CH<sub>4</sub>, leading to enrichment of <sup>13</sup>C in the remaining



**Figure 3.** Stable-carbon isotope ratios for  $\text{CH}_4$  plotted versus soil gas concentrations for  $\text{CH}_4$  at 2, 6, 11, and 12 m bgs for samples collected during injection (Day 0–5), post injection (Day 5–35), and on Day 400. Injected natural gas had a constant  $\delta^{13}\text{C}-\text{CH}_4$  value of  $-45\text{‰}$ .

$\text{CH}_4$  and  $^{12}\text{C}$  enrichment in the newly produced  $\text{CO}_2$  that is added to the large soil gas  $\text{CO}_2$  pool. The  $^{13}\text{C}$  enrichment in the remaining  $\text{CH}_4$  and the resulting  $\delta^{13}\text{C}-\text{CH}_4$  values between  $-42\text{‰}$  and  $+3\text{‰}$  provide strong evidence for partial  $\text{CH}_4$  oxidation in the vadose zone following the simulated natural gas injection. However, eight samples collected during injection were indicative of a microbial source of  $\text{CH}_4$  with  $\delta^{13}\text{C}-\text{CH}_4$  values between  $-69\text{‰}$  and  $-52\text{‰}$  (Figure 3) and low  $\text{CH}_4$  concentrations (up to 5% v/v). Microbially produced  $\text{CH}_4$  from acetate fermentation or  $\text{CO}_2$  reduction is expected to have  $\delta^{13}\text{C}-\text{CH}_4$  values between  $-110\text{‰}$  and  $-50\text{‰}$  (Golding et al., 2013; Schoell, 1988; M. J. Whiticar, 1999), more negative than the injected  $\text{CH}_4$  ( $-45\text{‰}$ ). The microbially produced  $\text{CH}_4$  may be from stagnant anaerobic regions displaced during the injection of the simulated natural gas. Values of  $\delta^{13}\text{C}-\text{CO}_2$  became enriched in  $^{12}\text{C}-\text{CO}_2$ , shifting from that of the injected gas ( $-11\text{‰}$ ) to as low as  $-27\text{‰}$ . However, the effect of  $\text{CH}_4$  oxidation is difficult to isolate based on  $\delta^{13}\text{C}-\text{CO}_2$  data alone, as the majority of samples (i.e., 66%,  $n = 109$ ) were influenced by the  $\delta^{13}\text{C}-\text{CO}_2$  signature from degradation of soil organic matter with baseline values between  $-23\text{‰}$  and  $-21\text{‰}$  (Figure S7 in Supporting Information S1).

Following the method proposed by Dixon and Romanak (2015), we plotted concentrations of  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{N}_2$  versus  $\text{CH}_4$  (% v/v) with mixing lines between baseline soil gas and injected natural gas (Figure S8 in Supporting Information S1). Subsurface gas concentrations during and post injection are dominated by mixing between baseline and injected gas. However,  $\text{CH}_4$  oxidation is also evident by some soils gas samples plotting off the mixing line (Figure S8 in Supporting Information S1).

#### 4. Conceptual Model

Characterizing the physical and biogeochemical processes that affect GM in the subsurface is necessary to understand the spatiotemporal variability of fugitive gas effluxes from oil and gas wells and to optimize monitoring approaches. While concentration gradients typically suggest that diffusion is the main gas-transport mechanism in the vadose zone, pressure gradients introduced for example, through the back pressure of natural-gas leakage or barometric-pressure changes, can result in faster bulk gas transport through advective GM. The deep vadose zone at our experimental field site led to barometric pumping to be a primary control on GM; however, differences in grain-size distribution also revealed that a low-permeability sediment barrier and a preferential pathway influenced gas transport and fate. During the natural-gas injection 12 m bgs, gas accumulated below the low-permeability sediment barrier until an interval of decreasing barometric pressure occurred (first seen on Day 3). The pressure gradient between the atmosphere and subsurface led to advective gas transport through the silt and clay materials, with preferential GM forming a  $\text{CH}_4$  hot spot on the ground surface (Figure S9 in Supporting Information S1). Although natural gas was actively released into the subsurface, an increase in barometric pressure led to a suppression of vertical GM with a rapid decline in  $\text{CH}_4$  effluxes and lateral expansion

of the subsurface CH<sub>4</sub> plume (Figure S9 in Supporting Information S1). The low-permeability sediment barrier combined with stages of increasing barometric pressure increased the residence time of CH<sub>4</sub> in the vadose zone, allowing gas to migrate beyond the monitoring network and promoting the progressive oxidation of CH<sub>4</sub> over time. This observation demonstrates that given a sufficiently long residence time in near surface zones that contain O<sub>2</sub>, fugitive gas released from oil and gas wells can be effectively attenuated by CH<sub>4</sub> oxidation, mitigating GHG emissions to the atmosphere. In this case, enhancing retention in the subsurface may be a potential remedial strategy to limit fugitive CH<sub>4</sub> emissions to the atmosphere. However, if fugitive gas is trapped below low permeability sediments, it is important to consider that the gas may migrate beyond typical monitoring networks focused around the wellhead.

The observed spatiotemporal trends in CH<sub>4</sub> effluxes were influenced by the lithology, barometric-pressure fluctuations, preferential flow channels and attenuation processes. Similar physical and biogeochemical processes may influence fugitive GM and spatiotemporal variability in CH<sub>4</sub> effluxes at other sites with leaking wells. To accurately detect and monitor GM, it is important to understand site-specific conditions at the time of assessment and to evaluate the potential for these processes to influence gas transport and fate. Current monitoring practices that rely on measurements in close proximity to an oil and gas wellhead during a one-time monitoring event (Alberta Energy Regulator, 2021; BC Oil and Gas Commission, 2018; Fleming et al., 2021; Forde, Mayer, & Hunkeler, 2018) may over- or underestimate, or not detect GM and GHG emissions. As studies advance knowledge on the processes influencing fugitive GM in the vadose zone, efforts should be made to improve monitoring protocols. Our findings have direct implications to improve detection and monitoring strategies for fugitive GM and for development of remedial techniques to limit environmental and climate impacts from leaking wells. In the presence of a deep vadose zone, comprehensive monitoring should include continuous measurements of barometric pressure as well as quantifying soil gas and CH<sub>4</sub> effluxes at frequent intervals and a high spatial resolution across the well site (not just immediately at the wellhead). Continuous monitoring not only allows for better detection and quantification of GHG emissions, but also provides insight into external factors that can control the variability and magnitude of CH<sub>4</sub> emissions.

## Abbreviations

bgs	below ground surface
GHG	greenhouse gases
GM	gas migration
IRGA	infra-red gas analyzer
SA	surface area
UGGA	Ultraportable Greenhouse Gas Analyzer

## Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

## Data Availability Statement

Processed data supporting this research is available in the Zenodo repository (<https://doi.org/10.5281/zenodo.6728352>).

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