Hydro-biogeochemical impacts of fugitive methane on a shallow unconfined aquifer

Olenka N. Forde, Aaron G. Cahill, K. Ulrich Mayer, Bernhard Mayer, Rachel L. Simister, Niko Finke, Sean A. Crowe, John A. Cherry, Beth L. Parker

PII: S0048-9697(19)32895-5
DOI: https://doi.org/10.1016/j.scitotenv.2019.06.322
Reference: STOTEN 32976
To appear in: Science of the Total Environment

Received date: 12 April 2019
Revised date: 20 June 2019
Accepted date: 20 June 2019

Please cite this article as: O.N. Forde, A.G. Cahill, K.U. Mayer, et al., Hydro-biogeochemical impacts of fugitive methane on a shallow unconfined aquifer, Science of the Total Environment, https://doi.org/10.1016/j.scitotenv.2019.06.322

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Hydro-Biogeochemical Impacts of Fugitive Methane on a Shallow Unconfined Aquifer

Olenka N. Forde\textsuperscript{1}, Aaron G. Cahill\textsuperscript{2,1,3}, K. Ulrich Mayer\textsuperscript{1}, Bernhard Mayer\textsuperscript{4}, Rachel L. Simister\textsuperscript{1,5}, Niko Finke\textsuperscript{1,5}, Sean A. Crowe\textsuperscript{1,5}, John A. Cherry\textsuperscript{2}, Beth L. Parker\textsuperscript{2}

1. Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, 2020-2007 Main Mall, Vancouver, BC, V6T 1Z4, Canada

2. G360 Institute for Groundwater Research, College of Engineering and Physical Sciences, University of Guelph, 50 Stone Road East, Guelph, ON, N1G 2W1, Canada

3. Heriot-Watt University, Lyell Centre, Research Avenue South, Edinburgh, EH14 4AP, United Kingdom

4. Department of Geoscience, University of Calgary, 2500 University Drive NW, Calgary, AB, T2N 1N4, Canada

5. Department of Microbiology and Immunology, University of British Columbia, 2350 Health Sciences Mall, Vancouver, BC, V6T 1Z3, Canada

*Corresponding author (oforde@eoas.ubc.ca)

Highlights

1. Two biogeochemical stages evolved during and post natural gas injection
2. Gas injection led to upward displacement of groundwater with elevated TDS
3. Dissolved methane persisted in groundwater >700 days post natural gas release
4. Aerobic and anaerobic methane oxidation was limited and spatially discrete
5. pH and geochemical changes were limited by carbonate mineral dissolution

Abstract
Oil and gas development can result in natural gas migration into shallow groundwater. Methane (CH₄), the primary component of natural gas, can subsequently react with solutes and minerals in the aquifer to create byproducts that affect groundwater chemistry. Hydro-biogeochemical processes induced by fugitive gas from leaky oil and gas wells are currently not well understood. We monitored the hydro-biogeochemical responses of a controlled natural gas release into a well-studied Pleistocene beach sand aquifer (Canadian Forces Base Borden, Ontario, Canada). Groundwater samples were collected before, during, and up to 700 days after gas injection and analyzed for pH, major and minor ions, alkalinity, dissolved gases, stable carbon isotope ratios of CO₂ and CH₄, and microbial community composition. Gas injection resulted in a dispersed plume of free and dissolved phase natural gas, affecting groundwater chemistry in two distinct temporal phases. Initially (i.e. during and immediately after gas injection), pH declined and major ions and trace elements fluctuated; at times increasing above baseline concentrations. Changes in the short-term were due to invasion of deep groundwater with elevated total dissolved solids entrained with the upward migration of free phase gas and, reactions that were instigated through the introduction of constituents other than CH₄ present in the injected gas (e.g. CO₂). At later times, more pronounced aerobic and anaerobic CH₄ oxidation led to subtle increases in major ions (e.g. Ca²⁺, H₄SiO₄) and trace elements (e.g. As, Cr). Microbial community profiling indicated a persistent perturbation to community composition with a conspicuous ingrowth of taxa implicated in aerobic CH₄ oxidation as well anaerobic S, N and Fe species metabolism.

Forde et al., 2018 STOTEN
Keywords
aqueous geochemistry; gas migration; groundwater; hydro-biogeochemistry; methane; natural gas; methane oxidation.

Abbreviations
bgs, below ground surface; CFB, Canadian Forces Base; DOC, dissolved organic carbon; EC, electrical conductivity; GM, gas migration; ID, inside diameter; M1-31, multilevel well 1-31; MCL, maximum contaminant level; PE, polyethylene; TDS, total dissolved solids; TIC, total inorganic carbon.

1. Introduction
Recent increases in shale gas development, conducted by horizontal drilling and hydraulic fracturing, have drawn attention to the issue of subsurface gas leakage from compromised oil and gas wells (CCA, 2014; Dusseault and Jackson, 2014; Vidic et al., 2013). Natural gas can escape from a wellbore casing and result in fugitive gas migration (GM) in the surrounding geologic material (Cahill et al., 2019). Gas migration can also arise during drilling if pathways are formed along the wellbore, mobilizing non-target reservoir gas at an intermediate depth (i.e. non-economic gas-rich strata between a target petroleum reservoir and shallow groundwater resources) (Dusseault and Jackson, 2014). Although well leakage has been historically documented and investigated (Dyck and Dunn, 1986; Gurevich et al., 1993; Harrison, 1983;
Kelly et al., 1985), the debate on the occurrence and impacts of GM has been re-ignited with the advent of shale gas development. In addition to creating a potential explosion hazard (Kelly et al., 1985; Williams and Aitkenhead, 1991), a primary concern related to GM is for natural gas constituents (i.e. methane (CH₄), ethane (C₂H₆) and propane (C₃H₈)) to ingress into aquifers containing potable groundwater and induce hydro-geochemical changes (Vengosh et al., 2014; Vidic et al., 2013). For the most part, recent research on fugitive gas and groundwater has taken an environmental forensics approach aiming to identify the origins of CH₄ in groundwater around regions of oil and gas development (Darrah et al., 2014; Humez et al., 2016a; Li and Carlson, 2014; Molofsky et al., 2016). However, few studies have specifically focused on the direct or indirect impacts of fugitive gas on aqueous geochemistry and the mechanisms by which they occur.

While dissolved CH₄ (CH₄(aq)) itself is non-toxic in drinking water, it can be utilized as a carbon source in microbial metabolic pathways causing the release of major ions and trace elements that can negatively affect water chemistry (Gorody, 2012). Such microbially mediated reactions occur based on availability of electron acceptors and their thermodynamic favourability (i.e. in order of the redox sequence, Table S1) (Christensen et al., 2000). These redox reactions also apply to C₂H₆ and C₃H₈ (Table S1). If dissolved oxygen (O₂(aq)) is present in groundwater, aerobic oxidation of CH₄(aq) will proceed first and produce dissolved carbon dioxide (CO₂(aq)) and water. Carbonic acidification, from CO₂(aq) generation, is well known to affect groundwater chemistry by inducing dissolution of acid soluble/reactive minerals and the release of undesirable trace elements (Cahill et al., 2014; Cahill and Jakobsen, 2013). Once O₂(aq) is depleted, or in the case of anoxic groundwater systems where none is present, CH₄(aq) oxidation can be coupled to less energetically favorable electron acceptors. Anaerobic CH₄(aq) oxidation involves reduction of
other dissolved species and/or reductive dissolution of solid phases present in the aquifer matrix (i.e. NO$_3^-$, Mn/Fe oxides and/or SO$_4^{2-}$, Table S1). These processes typically lead to an increase in alkalinity and other aqueous species byproducts (e.g. N$_2$(aq), H$_2$S(aq)/HS$^-$, Fe$^{2+}$, Mn$^{2+}$ and any associated trace elements), with impacts on water chemistry. In the field, anaerobic oxidation of fugitive CH$_4$(aq) has been observed and attributed to reduction of Fe- and Mn-oxides (Schout et al., 2017) and SO$_4^{2-}$ (Van Stempvoort et al., 2005; Wolfe et al., 2017). Anaerobic CH$_4$(aq) oxidation has also been observed in landfill leachate plumes (Christensen et al., 2000; Grossman et al., 2002) and aquifers contaminated with petroleum hydrocarbons (e.g.: Amos et al., 2012).

Although CH$_4$(aq) oxidation is generally well understood, more research is needed in the context of natural gas leakage to characterize the interacting processes that lead to fugitive CH$_4$ attenuation and/or secondary groundwater impacts.

Upward migration of deep saline fluids and entrainment with shallow potable groundwater could also contribute to deleterious changes in water chemistry around natural gas wells. Deep formation fluid migration to shallower groundwater has been observed in unconsolidated aquifers in the presence of faults (Bordeleau et al., 2018; Gumm et al., 2016). Studies have also measured elevated brine constituents (e.g. Na$^+$, Cl$^-$, Br$^-$) in groundwater wells around regions of shale gas development (Kreuzer et al., 2018; McPhillips et al., 2014; Warner et al., 2012; Yan et al., 2017). While various factors can contribute to saline groundwater in shallower aquifers, one possible explanation is the presence of pathways for deeper formation water to migrate vertically and become entrained with shallower water. However, it is currently difficult to attribute a direct link to oil and gas development and the mechanisms associated with such processes are not well characterized.
While concerns regarding fugitive CH$_4$ in groundwater persist, there remains limited knowledge of the hydro-biogeochemical processes that occur in aquifers during and after natural gas leakage. A controlled natural gas release experiment was recently conducted in a shallow unconfined aquifer at the Canadian Forces Base (CFB) Borden, Ontario, Canada. The experiment provided an opportunity to monitor the migration, impacts, and fate of simulated natural gas leakage in groundwater through a comprehensive multi-disciplinary approach (Cahill et al., 2017). Overall, it was shown that free phase gas was highly mobile in the unconsolidated, unconfined shallow aquifer. A relatively small volume release over a short timescale (i.e. 51 m$^3$ at standard temperature and pressure in 72 days) generated an extensive and dispersed plume of free and dissolved phase natural gas (Cahill et al., 2018, 2017; Forde et al., 2018; Steelman et al., 2017). Migration of the free phase gas, and consequently the volume of the impacted aquifer, were controlled by buoyancy and small-scale heterogeneities in sedimentary architecture. Vadose zone and surface efflux measurements up to day 87 indicate that at least half of the injected gas remained in the subsurface (Forde et al., 2018).

Here, we present high-resolution spatial aqueous chemistry data (including major ions, trace elements, alkalinity, dissolved gases and stable carbon isotope ratios of CO$_2$(aq) and CH$_4$(aq)) for samples collected before, during, and up to 700 days after the simulated natural gas release, and microbial community profiles from day 0-700. This paper follows a comprehensive review on the fate of dissolved gases during and shortly after injection (day 0 to 300) (Cahill et al., 2018) and reveals long-term trends (day 300 to 700) with secondary groundwater impacts. The objectives of this study were to: i) assess the long-term evolution of dissolved gases as a result of fugitive gas migration into a shallow unconfined aquifer; ii) characterize the occurrence and extent of fugitive CH$_4$ oxidation; iii) evaluate changes in aqueous geochemistry as a consequence
of fugitive gas migration and CH$_4$(aq) oxidation; and iv) discuss biogeochemical processes occurring in the short- and longer-term resulting from migration of fugitive gas into a shallow unconfined aquifer.

2. Materials and Methods

2.1 Field Site Geologic Setting

The natural gas release was conducted within CFB Borden, Ontario, Canada (Figure 1a). The aquifer at this site has been well characterized through previous studies on solid phase composition (Ball et al., 1990), groundwater flow (MacFarlane et al., 1983), hydrogeochemistry (Nicholson et al., 1983), and physical heterogeneity (Sudicky, 1986). The aquifer therefore provided a tractable setting to study the fate of natural gas through a controlled release experiment and associated hydrogeochemical impacts. In the experimental area within CFB Borden, the unconfined aquifer is composed of clean, well-sorted medium- to fine-grained silty sand with silt, silty clay, and coarse sand lenses underlain by a clayey silt aquitard and with a water table at ~1 m (fluctuating ± 0.5 m seasonally) below ground surface (bgs) (Sudicky and Illman, 2011). As part of the current study, a detailed interrogation of the sedimentary architecture was performed through depth-discrete grain size analyses on multiple cores, the results of which are described in detail by Steelman et al. (2017) and Cahill et al. (2018).

Historically, the aquifer material is documented to be dominated by calcareous sand with few clay minerals and low organic carbon content (0.02 to 0.09 %) (Ball et al., 1990; Mackay et al., 1986). Quartz is the predominant mineral followed by feldspar, carbonates, and to a lesser extent amphibole and chlorite (Mackay et al., 1986).
Studies from the 1980s categorized the aquifer into an upper uncontaminated region (from water table to ~7 m bgs), and a lower contaminated region (~8 m to 9 m bgs) due to the presence of a landfill-derived contaminant plume (Butler et al., 1997; MacFarlane et al., 1983). Groundwater in the uncontaminated aquifer was characterized by low levels of $O_{2(aq)}$ (<0.003 mmol L$^{-1}$, decreasing with depth), a narrow range in pH (6.8 to 8.0), total dissolved solids (TDS) ranging from 380 to 500 mg L$^{-1}$, electrical conductivity (EC, ~500 µS cm$^{-1}$), Cl$^-$ between 0.03 to 0.08 mmol L$^{-1}$, and $SO_{4}^{2-}$ ranging from 0.1 to 0.3 mmol L$^{-1}$ (Mackay et al., 1986; MacFarlane et al., 1983; Nicholson et al., 1983). Landfill contaminated groundwater was defined by elevated $SO_{4}^{2-}$ (9.6 mmol L$^{-1}$), Cl$^-$ (4.3 mmol L$^{-1}$), TDS (2300 mg L$^{-1}$), and EC (1500 µS cm$^{-1}$) (MacFarlane et al., 1983; Nicholson et al., 1983). The contaminant plume exhibited anoxic conditions as indicated by the presence of $Fe^{2+}$ (0.5 mmol L$^{-1}$) and $O_{2(aq)}$ below detection (1 µmol L$^{-1}$). The pH in the landfill leachate plume was similar to that of the uncontaminated water, ranging from 6.8 to 7.9 pH units (Nicholson et al., 1983). Present day, hydrogeologic conditions remain similar and the landfill leachate is still noticeable at the base of the aquifer (~7 m bgs and below). Notably, groundwater with elevated TDS is also common in regions of oil and gas development (Botner et al., 2018; Hildenbrand et al., 2015; Humez et al., 2016b). Therefore, the groundwater conditions found in the lower part of the Borden aquifer mimic those in aquifers that may be affected by fugitive GM.

2.2 Injection Infrastructure and Regime

Simulated natural gas (93.8 % CH$_4$, 3.8 % C$_2$H$_6$, 0.3 % C$_3$H$_8$, ~0.1 % C$_4+$, 1.1 % N$_2$, 0.8 % CO$_2$) was delivered to the subsurface through two 45$^\circ$ inclined sparging wells at depths of 4.5 m and 9 m bgs. The injected gas also contained a small amount of $O_2$ (0.05 %) introduced during
manufacturing of the gas mixture. Inclined sparging wells were used to minimize vertical GM along the injection tubing. The sparging wells were comprised of 1-m long porous polyethylene (PE) well screens [SCHUMASOIL®] connected to gas cylinders with 0.006 m (inside diameter [ID]) PE tubing, via a mass flow control-valve (Red-y smart GSC-C9SA-BB26) that was regulated by associated software (Get Red-y, Vögtlin Instruments AG, Switzerland). Over 72 days a total of 51 m$^3$ (at standard temperature and pressure) of simulated natural gas was injected at progressively increasing rates starting with the lowest rate of 0.2 m$^3$ day$^{-1}$ and ending with the highest rate of 4.3 m$^3$ day$^{-1}$ (Table S2). The injection rates were maintained continuously, except from day 38 to 42, when injection was interrupted due to a power outage on site. Injection wells were closed with non-return valves post injection.

2.3 Monitoring Network

Multilevel sampling wells were installed around the sparge wells and across the site using a Geoprobe (model 7822DT) direct push system. Each well was comprised of 0.006 m ID PE tubing with a 5-cm geotextile screen (Nitex monofilament screen cloth, 200 μm mesh) fixed to a polyvinyl-chloride center-stock. In total, 32 multilevel wells (M1 – M32, 122 sampling points) were screened at different intervals with either: three screens (2 m, 5 m and 8 m bgs); four screens (2 m, 4 m, 6 m, and 8 m bgs); or five screens (2 m, 3 m, 4 m, 5 m and 6 m bgs). Wells were spaced in ~1-m intervals around the injection location and then every 2 m, from 4 m to 10 m in the direction of groundwater flow (Figure 1b and 1c). In general, it is inevitable that sampling will influence flow paths in a groundwater system, particularly when there are 122 depth discrete sample points in an aquifer volume of ~350 m$^3$ (i.e. a high density of sampling points). However, the depth-discrete multilevel system with small diameter tubing (and low
volumes of groundwater extracted) was designed to minimize sampling-induced mixing of groundwater from different depths and to reduce any influence on the natural flow regime.

2.4 Analyses

Groundwater samples were collected from multi-level wells before, during and after (up to 700 days post injection) the introduction of natural gas into the aquifer. In addition to presenting previously unpublished geochemical and microbial data, this manuscript introduces new dissolved gas concentration and stable carbon isotope ratio data for samples from days 500 and 700, beyond those from Cahill et al. (2018).

Select field parameters were measured using a multi-parameter sonde and flow-through cell (Manta 2, Eureka Water Probes) supplied by a peristaltic pump at a flow rate of 40 to 50 mL min\(^{-1}\). Measurements included EC (±1 \(\mu\)S cm\(^{-1}\)), pH (± 0.1), temperature (± 0.02 \(^\circ\)C) and \(O_2(aq)\) (± 0.02 mg L\(^{-1}\) for low \(O_2(aq)\) range). The instrument was calibrated prior to each sampling campaign as per the manufacturer’s guidelines. The EC meter was calibrated with a 1413 \(\mu\)S standard solution and pH was calibrated with pH 7 and 10 buffer solutions. The instrument was equipped with an optical \(O_2(aq)\) sensor, known for very low drift in the field. The sonde auto-compensates for temperature (based on inbuilt temperature measurements for the sample). Dissolved gas samples were taken by submerging 40 mL volatile organic analysis vials in a beaker of sampled water immediately after sample collection and sealing the vials with septa caps leaving no headspace. Samples were stored upside down (to minimize potential gas exchange through the cap) at 4 \(^\circ\)C and analyzed for \(CH_4(aq), C_2H_6(aq), C_3H_8(aq), CO_2(aq),\) and \(N_2(aq)\) typically within 7 days, but no longer than 4 weeks after collection to minimize microbially mediated reactions in samples that were not treated with a biocide. The static headspace equilibrium technique
(Kampbell et al., 1989) was used to separate dissolved gases from water before analysing gas concentrations on a Bruker 450 Natural GC with measurement uncertainties of ± 5% of the analyte. Although dissolved gas sampling with a peristaltic pump and the semi-open sampling method can result in degassing, appropriate steps were taken to minimize gas loss (e.g. low pumping rates and short tubing lengths). Due to the possibility of degassing, dissolved gas concentrations reported here should be considered conservative and might be higher in-situ. However, potential loss of dissolved gases does not interfere with the interpretations and conclusions of this manuscript, which mainly focus on changes in groundwater chemistry related to major ion and trace element concentrations, microbial community profiling, and stable carbon isotope ratios.

Samples for major and minor cations were filtered (0.45 µm cellulose acetate filters) and acidified (concentrated HNO₃) in the field and stored at 4 °C until analyses. Samples were analyzed on an Agilent 8800 Inductively Coupled Plasma Triple Quad Mass Spectrometer using the NIST SRM 1640a (Trace Elements in Natural Water) and CALA CO2A elements (full range) in water (Proficiency Testing Program) standards for QC/QA. Measured concentrations were within 5% of the certified values (see Table S3 for detection limits). Samples for major anions (Cl⁻, NO₃⁻ and SO₄²⁻) were collected unfiltered and concentrations were determined using a Dionex ICS 2000 ion chromatograph (Dionex Corporation). A 25 µL aliquot of each sample was injected onto an Ion Pac AS18 anion column (Dionex Corporation) and then separated by isocratic elution using 35 mM potassium hydroxide, a flow rate of 1 mL min⁻¹, and a column temperature of 30 °C. Analytical precision and accuracy for anion analysis was ± 5%. Alkalinity was determined in the field (by Gran titration) for selected samples.
Samples for analysis of stable carbon isotope ratios ($^{13}$C/$^{12}$C) of CH$_4$(aq) and CO$_2$(aq) were obtained by piercing the septa of pre-evacuated 125 mL glass vials that were filled by submerging them into a continuously filling sample container. Vials were treated with 20 μL of a biocide (mercuric chloride [HgCl$_2$]). The samples were stored at 4 °C prior to analysis using the static headspace equilibrium technique (Kampbell et al., 1989) to separate dissolved gases from water. Subsequently, headspace gas was injected into a gas chromatograph (GC) and carbon isotope ratios of CO$_2$(aq) and CH$_4$(aq) (after conversion to CO$_2$(aq) and cryo-focussing) were determined with a ThermoFisher MAT 253 isotope ratio mass spectrometer (IRMS) coupled to a Trace GC Ultra + GC Isolink (ThermoFisher) at the Isotope Science Laboratory at the University of Calgary (Alberta, Canada). Carbon isotope ratio measurements of CO$_2$(aq) were bracketed and normalized using two calibration gases with widely different $\delta^{13}$C values (Oztech -3.6 and -48 ‰) that were anchored against international reference materials. For CH$_4$(aq), additional reference gases from Scott ($\delta^{13}$C of -69 and -25 ‰) and Isometric ($\delta^{13}$C of -67, -38 and -24 ‰) were used to ensure complete conversion of CH$_4$(aq) to CO$_2$(aq) prior to mass spectrometric analyses and accurate $\delta^{13}$C values for CH$_4$(aq). Results are reported in the internationally accepted delta ($\delta^{13}$C) notation (in ‰) relative to VPDB with a precision better than ± 0.5 ‰ and ± 0.3 ‰ for $\delta^{13}$C values of CH$_4$(aq) and CO$_2$(aq), respectively.

2.5 Geochemical Modeling

Geochemical modeling was conducted with Phreeqc Interactive (Version 3.4.0-12927 using the wateq4f database) to quantitatively evaluate water chemistry data with a focus on mineral solubility controls and to bracket hydrogeochemical changes. To determine saturation states for
select mineral phases at 2 m, 6 m, and 8 m bgs, speciation calculations were performed based on hydrogeochemical conditions (major ions, alkalinity, pH and temperature) before, during, and after injection from groundwater collected in a well near the injection location (M7, Table S4). Oxides containing oxidized forms of Fe and Mn were not included in the modeling due to uncertainties in aqueous redox equilibria.

Typically, hydrodynamic dispersion does not cause extensive mixing of groundwater and solutes in an aquifer. However, injection of free-phase gas could invoke mixing in two ways: 1) gas partitioning between dissolved gases present in the groundwater and gases constituting the free-phase injected gas and; 2) entrainment of deeper groundwater with upwards-migrating free-phase gas to shallower depths. Geochemical modeling was used to investigate the extent and impacts of these mixing processes along with CH₄ oxidation. To bracket the range of effects on pH and associated hydrogeochemical changes, all gas partitioning and reaction path simulations were performed with and without calcite equilibration.

The injected natural gas contained small amounts of O₂(g) and CO₂(g) (0.05 % and 0.8 %, respectively). Therefore, gas partitioning simulations were performed to assess pH and hydrogeochemical changes associated with O₂(g) and CO₂(g) dissolution into groundwater and, subsequent CH₄(aq) oxidation by O₂(aq). For these simulations, a gas phase mimicking the composition of the simulated natural gas injected during the field experiment (only containing CH₄, N₂, and either O₂ or CO₂) was introduced to baseline groundwater from M7 (Table S4 and Table S5). Natural gas constituents C₂H₆ and C₃H₈ were included in the initial analysis, but were not further considered since their presence had no noticeable impact on groundwater pH. When present, O₂(aq) was allowed to oxidize CH₄(aq), while CH₄(aq) oxidation by other electron acceptors, such as SO₄²⁻ or NO₃⁻, was excluded from these simulations. Gas partitioning
simulations were completed for 2 m, 6 m, and 8 m depths starting with baseline conditions from M7 for major ions, alkalinity, pH and temperature (Table S4). Gas phase pressures were fixed, dependent on the depth below the water table and, an initial water:gas volume ratio of 1:1 was assumed.

Our second mixing hypothesis was that deep groundwater could be entrained during the upward migration of the injected free phase gas and be displaced into shallower groundwater. To investigate the potential impacts caused by mixing of the displaced deep groundwater with shallower groundwater, Phreeqc simulations were performed where groundwater from depths of 2 m and 6 m, as well as 6 m and 8 m were mixed. For these simulations average baseline conditions for groundwater collected at M7 (Table S4) from depths of 2 m and 6 m, as well as 6 m and 8 m were mixed at ratios ranging from 0.1 to 0.9.

Geochemical changes in groundwater related to CH$_4$(aq) oxidation with select electron acceptors (Table S1) were evaluated through reaction path simulations. Baseline groundwater from M7 (Table S4) was titrated with CH$_4$(aq) (1.3 mmol L$^{-1}$) to mimic the injection of CH$_4$ present in the natural gas. Over 20 steps, one electron acceptor was isolated to react with the injected CH$_4$. Redox-active species not directly targeted in the simulations were decoupled to avoid the enforcement of unwanted redox equilibria complicating interpretation of the results (Table S4). The initial concentration of the electron acceptors was defined using baseline conditions at each depth from which groundwater was obtained (Table S4).

2.6 Microbial Community Profiling
Microbial biomass was collected from groundwater as described in Kenward et al. (2018). Environmental DNA was extracted from recovered biomass using DNeasy PowerSoil Kit (Qiagen) as per manufacturer’s instructions. Resulting DNA was stored at -20 °C. Quantification was conducted using the PicoGreen® Assay (Invitrogen) for dsDNA (Singer et al., 1997), measured on a TECAN™ M200 (excitation at 480 nm and emission at 520 nm) (Table S6). Purity and quality of DNA was assessed based on ratios for A_{260}/A_{280} measured using a NanoDrop® ND-1000 spectrophotometer (Thermo Scientific). The V4-V5 region of the small subunit rRNA gene was amplified and sequenced, and the resulting sequence information processed using standard bioinformatic analyses to generate microbial community composition profiles (see SI Section 1 for details).

3. Results and Discussion

3.1. Baseline conditions

Prior to natural gas injection, CH$_4$(aq) concentrations were naturally very low at all depths (ranging from 0.0001 to 0.02 mmol L$^{-1}$, Table S7). Stable carbon isotope analyses indicated a microbial origin of CH$_4$ with $\delta^{13}$C values as low as -80 ‰ but also signs of CH$_4$(aq) oxidation resulting in $\delta^{13}$C-CH$_4$ values as high as -47 ‰. Average CO$_2$(aq) increased with depth, up to 2.5 mmol L$^{-1}$ at 8 m bgs. Baseline $\delta^{13}$C-CO$_2$ values of -21 ‰ were measured at 2 m and 5 m depths. Dissolved N$_2$ varied over depth with concentrations ranging from 0.2 to 0.7 mmol L$^{-1}$ (Table S7).

Two distinct hydrogeochemical zones were observed within the 8 m thick aquifer: an upper zone with fresh water and low TDS and hence EC (from water table to ~7 m depth) and, a thin zone at the base of the aquifer containing water with higher EC (8 m to 9 m depth).
Groundwater in the lower zone (8 m to 9 m depth) remains affected by the leachate from the construction waste landfill, as reported by McFarlane et al. (1983), as discussed in Section 2.1.

A shallow water table, as at our field site (~1 m bgs), can lead to incomplete oxidation of dissolved organic carbon (DOC) in the vadose zone. As a result, recharging groundwater through the vadose zone introduced DOC into the shallow aquifer (i.e. 2 m to 4 m bgs). Subsequent oxidation of DOC in the shallow aquifer caused mildly reducing conditions and low \( \text{O}_2(\text{aq}) \) concentrations (< 0.01 mmol L\(^{-1}\)) under baseline conditions. Deeper in the aquifer (6 m to 8 m depths), \( \text{O}_2(\text{aq}) \) concentrations decreased below the limit of detection (< 0.001 mmol L\(^{-1}\), not shown), due to stronger reducing conditions caused by higher DOC content in the landfill leachate. Lower pH values (as low as 6.7 pH units) and higher alkalinities (up to 7.7 meq L\(^{-1}\)) were observed 6 m to 8 m bgs. However, pH was in general circumneutral at all depths (Table S7). The fresh groundwater in the upper zone (2 m to 6 m) was characterized by lower EC values (324 to 795 \( \mu \text{S cm}^{-1} \)) than in the deeper aquifer (1086 to 2433 \( \mu \text{S cm}^{-1} \) at 8 m bgs, Table S7). Elevated EC 8 m bgs is attributed to the higher concentrations of \( \text{Cl}^- \), \( \text{SO}_4^{2-} \), \( \text{Ca}^{2+} \), \( \text{Fe}^{2+} \), \( \text{Mg}^{2+} \), \( \text{Na}^+ \) and \( \text{H}_4\text{SiO}_4 \) (Table S8). In general, there was variability in the baseline ranges of major and minor cation and anion concentrations. However, the ranges were comparable between shallow depths (2 m to 6 m) and higher 8 m bgs (Tables S8 and S9).

### 3.2. Evolution of dissolved gases

During and following injection, a strong correlation was observed for groundwater concentrations of \( \text{CH}_4(\text{aq}) \) with \( \text{C}_2\text{H}_6(\text{aq}) \) and \( \text{C}_3\text{H}_8(\text{aq}) \) (correlation coefficients > 0.9, Cahill et al., 2018). The evolution of \( \text{CH}_4(\text{aq}) \) is therefore representative for the behavior of all dissolved hydrocarbons. Cahill et al. (2018) provides a detailed description on the evolution of dissolved
gases; however, only up to day 300 of the experiment. In general, higher silt and clay contents between 2.5 m and 4 m bgs (Steelman et al., 2017) affected GM and led to greater average CH$_4$(aq) concentrations during and after injection (>0.006 mmol L$^{-1}$) at 2 m, 6 m, and 8 m bgs compared to those monitored directly above the lower permeability lenses (e.g. 4 m bgs, Figure S1). Horizons at 2 m, 6 m, and 8 m depth are thus most suitable to assess potential impacts of fugitive CH$_4$ on long-term hydrogeochemical changes. Dissolved gas concentration trends at individual monitoring locations (M1-M32) were similar to trends for composite dissolved gas concentrations representing averages of all locations for each respective depth. Spatially averaged concentrations values for dissolved gases are therefore used to document long-term temporal changes at depths of 2 m, 6 m, and 8 m over a larger representative area of aquifer.

For the entire duration of monitoring (i.e. up to 700 days after start of injection), average CH$_4$(aq) remained above baseline levels at depths of 2 m, 6 m, and 8 m (Figure 2). During active injection (day 0 to 72), CH$_4$(aq) fluctuated at all depths with random events that led to marked increases in CH$_4$(aq) concentrations at depth. Elevated concentrations at 2 m and 6 m led to lateral GM in the direction of groundwater flow and down gradient of the injection screens (Figure 2 and S1). At 2 m depth, the greatest increase in average CH$_4$(aq) occurred from day 7 to 14, rising from 0.04 to 0.2 mmol L$^{-1}$, after which concentrations remained > 0.2 mmol L$^{-1}$ to day 700. At 6 m bgs, the greatest increase in average CH$_4$(aq) was from 0.003 mmol L$^{-1}$ on day 14 to 0.2 mmol L$^{-1}$ on day 28, after which concentrations remained elevated (>0.3 mmol L$^{-1}$) until day 300 (Figure 2). At 8 m bgs, average CH$_4$(aq) increased on day 21 and remained >0.03 mmol L$^{-1}$ until day 127. Episodic increases in CH$_4$(aq) can be attributed to CH$_4$ dissolution following gas phase breakthrough driven by pore scale heterogeneities. Although the Borden aquifer is primarily comprised of fine sand, a detailed analysis of grain-size distribution at the field-site revealed
variations in grain size with laminations containing higher contents of silts and clay within fine sand layers. Lower permeability layers within the fine sand were identified between 2.5 m and 4 m bgs and from ~7.5 m to 9 m bgs. Between these layers were more coarse and medium sands containing some pebbles within the fine sand (Steelman et al., 2017). Due to buoyancy forces, gas phase CH$_4$ accumulated below the capillary barriers containing increased fine sand, silt and clay contents, until overcoming the entry pressure for breakthrough. Gas breakthrough resulted in dissolution of CH$_4$ in the overlying layers and/or migration to the vadose zone and atmosphere (Cahill et al., 2018; Forde et al., 2018; Steelman et al., 2017). Surface efflux and soil gas measurements demonstrated that CH$_4$ was intermittently released to the atmosphere due to episodic gas breakthrough from the saturated zone (Forde et al., 2018).

At all depths, maximum CH$_4$(aq) concentrations were observed shortly after the injection stopped (day 77 to 113, Figure 2 and S1). The increase in concentrations is due to the loss of external (gas injection) pressure that had enabled the free phase gas buoyancy forces to overcome capillary forces. When injection stopped, free phase gas became trapped in place and inflowing groundwater promoted dissolution of gas bubbles. Dissolved CH$_4$ remained in the aquifer up to day 700 where CH$_4$(aq) concentrations were the highest at 2 m depth (average of 0.2 mmol L$^{-1}$ and up to 0.6 mmol L$^{-1}$), followed by concentrations at 6 m (average of 0.01 mmol L$^{-1}$ and up to 0.02 mmol L$^{-1}$) and 8 m (average of 0.008 mmol L$^{-1}$ and up to 0.2 mmol L$^{-1}$) depths (Figure 2). Although CH$_4$(aq) began to decrease towards the end of the experimental monitoring period, concentrations were still above baseline. Persistence of elevated CH$_4$(aq) on day 700 (up to 0.6 mmol L$^{-1}$ at 2 m bgs) is indicative of continued dissolution of entrapped gas. However, the decline in concentrations also suggest the occurrence of oxidation (see Section 3.3), flushing and/or dilution.
Average CO$_2$(aq) concentrations at depths of 2 m and 6 m were above baseline (by 0.2 mmol L$^{-1}$) during injection, but then declined until the end of monitoring (day 700), with the exception of an increase on day 500 (Figure 2). At 2 m bgs, the greatest increases in CO$_2$(aq) (to 0.7 mmol L$^{-1}$) were observed at the same location (M7) where some of the highest CH$_4$(aq) concentrations were detected (up to 1.8 mmol L$^{-1}$). The same correlation of locations with highest CO$_2$(aq) and elevated CH$_4$(aq) was observed at 6 m bgs. The increase in CO$_2$(aq) may be due to CH$_4$ oxidation. At 8 m depth, aside from day 14, CO$_2$(aq) slightly decreased below baseline (by up to 0.6 mmol L$^{-1}$). The decline in CO$_2$(aq) can be attributed to stripping of CO$_2$ due to the natural gas injection. Stripping likely only occurred at 8 m due to the fact that this sampling depth is closer to the injection well (at 9 m) than the 6 m and 2 m sampling ports, and is thus more directly influenced by the natural gas release.

Similar to the stripping of CO$_2$(aq) at 8 m depth, N$_2$(aq) concentrations decreased below baseline values at all depths during and shortly after the injection (day 0 to 120). Stripping of N$_2$(aq) further supports the existence of a dynamic system with free phase CH$_4$ migration. However, towards the end of the monitoring period, N$_2$(aq) concentrations increased above baseline from 0.6 mmol L$^{-1}$ to 2.4 mmol L$^{-1}$ at 2 m bgs (Figure 2). Enrichment of N$_2$(aq) concentrations at late time may be indicative of near complete CH$_4$ dissolution, caused by flushing with CH$_4$-free groundwater and possibly enhanced by CH$_4$(aq) oxidation. Both CO$_2$ and CH$_4$ have higher solubilities than N$_2$ (effectively 33.6 mmol L$^{-1}$, 1.4 mmol L$^{-1}$, and 0.6 mmol L$^{-1}$, respectively at 298 K and 10$^5$ Pa). As a result, CH$_4$ and CO$_2$ preferentially dissolved from entrapped gas into the inflowing groundwater post injection. Simultaneously, N$_2$(aq) partitioned into the entrapped gas bubbles due to the naturally higher N$_2$(aq) in the inflowing groundwater, and thereby leading to an increase of N$_2$ in the residual gas bubbles. The residual gas bubbles
became progressively N₂ enriched due to CH₄ and CO₂ preferentially dissolving into CH₄-free and CO₂-poor ingressing groundwater, flushing and oxidation. Enrichment of N₂ in entrapped gas provided a driving force for N₂ dissolution into groundwater, explaining the observed elevated N₂(aq) concentrations at late time. A similar observation was also made in an aquifer experiment in Bitterfeld, Germany (Balcke et al., 2011). Denitrification may provide an alternative source for N₂, particularly at 6 m depth, where NO₃⁻ concentrations slightly decreased. However, N₂-enrichment at 8 m bgs coincided with a rise in NO₃⁻ concentrations, and NO₃⁻ was generally below detection at 2 m depth (see Section 3.3 and Table S10), implying that dissolution from N₂-enriched gas bubbles provides a more likely explanation. Although N₂ stripping can be associated with fugitive GM (Cahill et al., 2018; Larson et al., 2018), we show here that enrichment in N₂(aq) can also be expected post wellbore leakage. Particularly, N₂ enrichment could be used as an indicator for substantial or near-complete removal of free-phase CH₄ from an aquifer.

3.3. Occurrence and extent of fugitive methane oxidation

3.3.1. Stable carbon isotope ratios
Natural attenuation of CH₄(aq) through oxidation depends on catalysis by the resident microbial community, which couples CH₄(aq) oxidation to the reduction of available terminal electron acceptors (Table S1) (Röling and van Verseveld, 2002; Scow and Hicks, 2005). Microbes preferentially oxidize CH₄(aq) containing the light isotope ¹²C resulting in a progressive enrichment of the heavier isotope ¹³C in the remaining CH₄(aq) (Barker and Fritz, 1981; Whiticar and Faber, 1986). Therefore, δ¹³C-CH₄ values higher than the injected natural gas (-42 ‰) can
be attributed to CH$_4$(aq) oxidation. From day 0 to 300, only eight of 114 samples displayed $^{13}$C enrichment compared to the injected CH$_4$ (Cahill et al., 2018). These samples were all from 8 m depth with $\delta^{13}$C-CH$_4$ values ranging from -40 ‰ to -33 ‰ and associated CH$_4$(aq) concentrations of 0.05 and 0.01 mmol L$^{-1}$, respectively. From day 300 to 700, 56 of 132 samples from all depths (except 3 m) had $\delta^{13}$C-CH$_4$ values more $^{13}$C-enriched than that of injected CH$_4$ ranging from -40 ‰ to +18 ‰ with associated CH$_4$(aq) of 1.0 and 0.002 mmol L$^{-1}$, respectively (Figure 3a). The greatest $^{13}$C-enrichment in remaining CH$_4$(aq) in groundwater throughout the entire experiment was observed at 8 m depth on day 500 with $\delta^{13}$C-CH$_4$ values ranging from -15 ‰ to +18 ‰ and CH$_4$(aq) < 0.006 mmol L$^{-1}$ (n = 9) (Figure 3a). The injected gas had a gas dryness (ratio of methane [C$_1$] to ethane [C$_2$] plus propane [C$_3$]) of ~23.4. From day 300 to 700, 53 of 64 samples retained this thermogenic signature (Figure 3b). Samples that were not enriched in $^{13}$C were either similar to the isotopic signature and concentration of background CH$_4$(aq) (e.g. -67 ‰ and CH$_4$(aq) of 0.006 mmol L$^{-1}$) or, at higher concentrations, most $\delta^{13}$C-CH$_4$ values were only slightly lower than that of the injected gas (e.g. -43 ‰ and CH$_4$(aq) of 0.6 mmol L$^{-1}$). Values where $\delta^{13}$C-CH$_4$ was lighter, more negative than the injected gas could be due to preferential fractionation of the light isotope ($^{12}$C) with diffusive migration (Chanton, 2005; Egger et al., 2015) and/or, mixing of background and injected CH$_4$ associated with gas partitioning between natural groundwater and injected gas. The greatest $^{12}$C-enrichment in CH$_4$(aq) was observed at 2 m depth, located vertically farthest away from the injection points at 9 m and 4.5 m, consistent with C-isotope fractionation of CH$_4$(aq) due to diffusive migration away from the injection locations (Figure 3). Two end member mixing calculations of background $\delta^{13}$C-CH$_4$ (-47 ‰ to -80 ‰) with injected $\delta^{13}$C-CH$_4$ (-42 ‰) led to $\delta^{13}$C-CH$_4$ values between -42 ‰ and -45 ‰. Therefore, samples with $\delta^{13}$C-CH$_4$ values lower than -45 ‰ and higher CH$_4$(aq) concentrations are likely
associated with both fractionation due to diffusive transport and C-isotope mixing with background CH$_4$. Overall, the much higher occurrence of $^{13}$C-enrichment in CH$_4$(aq) across the aquifer from day 300 to 700 indicates that the extent of CH$_4$(aq) oxidation substantially increased with time.

From day 50 to 700, $\delta^{13}$C-CO$_2$ decreased from baseline of -21‰ to values between -22‰ to -24‰ (Figure S2). Enrichment of $^{12}$C in CO$_2$(aq) and $^{13}$C in CH$_4$(aq) implies CH$_4$(aq) oxidation, primarily from day 300 to 700. Changes in $\delta^{13}$C-CO$_2$ were much smaller (at most 5‰) than those for $^{13}$C-CH$_4$ due to the high total inorganic carbon (TIC) content (up to 13 mmol L$^{-1}$) of background groundwater. High TIC minimizes changes in $\delta^{13}$C-CO$_2$ with CH$_4$(aq) oxidation and leads to relatively constant CO$_2$(aq) concentrations, as observed throughout the experiment at each depth (Figure 2). The variations of stable carbon isotope ratios over time and depth may imply a dynamic evolution of microbially mediated processes (aerobic versus anaerobic) involved in CH$_4$(aq) oxidation.

### 3.3.2. Microbial community profiling

Focusing on the most recent data from day 700, microbial community profiling revealed a relatively diverse assemblage of microorganisms (Figure S3) including taxa related to those with known metabolic potential for aerobic CH$_4$(aq) oxidation, as well as a single taxon related to Candidatus methylomirabilis, which is best known for its capacity to couple CH$_4$(aq) oxidation to denitrification (Figure S4). At day 700, the microbial community was comprised of between 441 and 1376 operational taxonomic units (OTU, 97% similarity) (SI Section 2) (Figure S5 and S6). From day 0 to 700, 46 taxa were identified related to organisms previously implicated in coupled
C, O$_2$(aq), N, Fe, and S cycling as well as CH$_4$(aq) and methylated compound metabolism (Figure S4). The most abundant organisms were related to those with known metabolic potential for methylotrophy, a diverse group of micro-organisms specialized on oxidizing reduced single carbon compounds, providing indirect evidence for CH$_4$(aq) oxidation (Figure S4). Organisms with potential for methanotrophy or NO$_3^-$ respiration were most abundant between 2 m and 4 m depths and their abundances increased rapidly with natural gas injection. Microorganisms known as SO$_4^{2-}$ reducers were also present, predominantly post injection at 8 m depth within the sulfate-rich groundwater affected by landfill leachate. Although organisms related to SO$_4^{2-}$ reducers were present at relatively low abundances, this group of microorganisms showed a relatively high degree of diversity (Figure S4, SI Section 2). Figure 4 also indicates that the ingrowth of organisms related to SO$_4^{2-}$ reducers proceeded relatively slowly in comparison to those related to methanotrophs and denitrifiers with the highest abundances and diversity seen at day 700. Organisms known to reduce Fe(III) were also present, but clear chemical evidence for iron respiration was sparse (Figure S4). Although the strongest isotopic evidence for CH$_4$(aq) oxidation occurred post injection, the microbial community adapted relatively quickly (first evidence on day 45) with a persistent perturbation to the composition. The diversity in organisms is comparable to previous analyses of shallow subsurface microbial communities (Gulay et al., 2016; Sang et al., 2018; Unno et al., 2015; Vosin et al., 2018) and this likely reflects microbial community metabolism through both aerobic CH$_4$(aq) oxidation and anaerobic respiration. The development of a microbial community capable of aerobic CH$_4$ oxidation could have been initiated through dissolution of O$_2$(g) introduced with the injected simulated natural gas, particularly in the anoxic environment at 8 m depth. Microbial evidence for aerobic CH$_4$(aq) oxidation in an anoxic environment does not preclude anaerobic CH$_4$(aq) oxidation. Rather, it
implies a complex interaction among micro-organisms, for which the analysis was beyond the scope of this paper.

3.3.3. Redox indicator species

Throughout the experiment average changes in concentrations of redox indicator species were subtle (Figure 4, typically <1 mmol L⁻¹), and did not provide clear evidence for the mechanism(s) of CH₄(aq) oxidation. Utilization of the various electron acceptors has been shown to affect groundwater pH in characteristic ways. Typically, pH decreases during aerobic respiration, increases with Fe(III)- and Mn(IV)-oxide reduction, and changes minimally during denitrification and bacterial SO₄²⁻ reduction (Appelo and Postma, 2004; Mayer et al., 2001). To further evaluate the contribution of the various electron-accepting processes to CH₄(aq) oxidation, reaction path simulations with Phreeqc were performed by titrating CH₄(aq) into baseline groundwater at various depths (Table S5). For each simulation, redox reactions were restricted to a single electron acceptor to isolate its contribution to pH changes. Simulation results indicated very limited pH changes consistent with those observed at the field site (<0.3 pH units) for CH₄(aq) oxidation coupled to aerobic respiration, denitrification and bacterial SO₄²⁻ reduction. However, the results also suggested that substantial Fe(III) and Mn(IV)-reduction would lead to marked increases in groundwater pH (>0.3 pH units), not observed in our experiment. These site-specific results confirm previous findings (Appelo and Postma, 2004; Mayer et al., 2001). However, slight increases of Fe²⁺ and Mn²⁺ concentrations could indicate that a minor amount of Fe(III) and Mn(IV) reduction did occur. Lower pH values despite the occurrence of reductive dissolution could be due to Fe²⁺ and Mn²⁺ sorption and deprotonation. Reactive transport
modeling of geochemical processes in a hydrocarbon contaminant plume in the Bemidji aquifer, United States of America, demonstrated that Fe\(^{2+}\) adsorption coupled with deprotonation provided a pH buffer to reduce secondary groundwater impacts (Ng et al., 2015). Nitrate and SO\(_4^{2-}\) concentrations fluctuated in unexpected ways; at times increasing above baseline concentrations indicating no consistent evidence for CH\(_4\)\(_{(aq)}\) oxidation coupled with the reduction of these electron acceptors (Figure 4 and Table S10). The fluctuation in redox indicator species indicates that their natural variability was enhanced by other mechanisms beyond CH\(_4\)\(_{(aq)}\) oxidation, over-printing changes that could otherwise be attributed to CH\(_4\)\(_{(aq)}\) oxidation. These changes are likely associated with physical processes occurring as a result of natural gas injection (see Section 3.4).

3.4. Hydrogeochemical changes as a consequence of fugitive gas migration and methane oxidation

3.4.1 Evolution of EC and pH

The natural gas injection led to perturbations of aqueous geochemistry as evidenced by changes in EC and pH. From day 0 to 300, EC ranged from 240 µS cm\(^{-1}\) (at 2 m bgs) to 844 µS cm\(^{-1}\) (at 6 m bgs), and generally increased at 2 m and 6 m depths during injection (Figure S7). There were four events when EC increased >100 µS cm\(^{-1}\) above baseline at depths of 2 m and 6 m (days 21, 28, 63 and 70) (Figure S7). After day 300, EC returned to baseline values in groundwater at 2 m and 6 m depths, ranging from 166 µS cm\(^{-1}\) (at 2 m) to 559 µS cm\(^{-1}\) (at 6 m). The observed sporadic increases in EC can be attributed to increases in SO\(_4^{2-}\) (Figure 4) and other major ions, particularly Na\(^+\) and Cl\(^-\) (Figure 5). When EC increased, the ion composition at 2 m bgs was similar to baseline groundwater at 6 m bgs and, the groundwater ion composition at 6 m bgs was
close to the baseline composition 8 m bgs (Figure 6a). The similarities between groundwater compositions from 6 m bgs and 8 m bgs (Figure 6) suggests that the landfill leachate at the base of the aquifer (8 m to 9 m depth) was entrained and pulled upward during episodic gas breakthroughs, contributing to temporary increases in EC (Figure S7).

Natural gas injection at 9 m depth led to an upward displacement of landfill leachate contaminated groundwater with TDS concentrations at least twice as high as in shallower uncontaminated groundwater. As gas migrated upward, driven by buoyancy forces, the entrained leachate impacted water-filled pore spaces and mixed with fresher groundwater. Mixing lines (modeled with Phreeqc) for $\text{SO}_4^{2-}$ and $\text{Cl}^-$ involving groundwaters from 2 m and 6 m depths, as well as 6 m and 8 m depths (Figure 6b) support the upward migration and mixing of deep more acidic water with shallow groundwater. Mixing led to a temporary rise of ion concentrations and contributed to the decrease in pH at depths of 2 m and 6 m from day 0 to 300 (Figure S8 and Table S10). Throughout the experiment, pH at depths of 2 m, 6 m and 8 m fluctuated around 7 by up to ± 0.3 pH units (Table S10). In the short-term (day 0 to 300), the average pH decreased in groundwater at depths of 2 m and 6 m by 0.3 and 0.1 pH units, respectively. Phreeqc mixing simulations demonstrate that a pH decrease by 0.2 pH units can be obtained in the shallower groundwater by entraining and mixing groundwaters from 6 m depth and 2 m depth (or groundwaters from 8 m depth and 6 m depth) at a 1:9 (shallow:deep groundwater) ratio. However, for both scenarios, the pH change is restricted to 0.1 pH units for a 1:1 mixing ratio, suggesting that entrainment of deeper water alone cannot fully explain the observed pH decreases. An additional process that can contribute to the observed pH decreases is the dissolution of $\text{CO}_2(\text{g})$ present in the natural gas at low concentrations. Gas partitioning simulations with Phreeqc showed that equilibrating natural gas containing 0.8 % $\text{CO}_2(\text{g})$ at a 1:1
volume ratio with baseline groundwater causes a pH decrease by up to 0.1 pH units at 2 m and 6 m depths (Table S5). As discussed above, aerobic CH$_4$(aq) oxidation is another process that can cause pH to decline. Aerobic CH$_4$(aq) oxidation may be driven by O$_2$(aq) present in shallow groundwater prior to injection or a small fraction of O$_2$ that was present in the injected gas (0.05 % O$_2$). Gas partitioning simulations accounting for the O$_2$ in the natural gas and allowing for its reduction by CH$_4$(aq) oxidation indicate only a small pH decline restricted to <0.02 pH units at depths 2 m and 6 m due to this process (Table S5). The negligible change in pH implies that the presence of O$_2$ in the injected gas was of minor importance to the redox environment, but may have contributed to the growth of organisms with known potential for methanotrophy (Figure S4). Although it is not possible to identify a specific process responsible for the observed pH decreases, a combination of entrainment and mixing, CO$_2$(g) dissolution, and CH$_4$(aq) oxidation likely caused the decline of pH in groundwater at 2 m and 6 m depth between days 0 to 300. It can be concluded that pH changes were minor (at times below measurement accuracy).

3.4.2. Distribution of major ions and trace elements

Major ion concentrations fluctuated over time, particularly during active injection. The greatest increases were observed for Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and H$_4$SiO$_4$ at 2 m, 6 m and 8 m depths, with less pronounced changes observed for Cl$^-$ and K$^+$ (Figure 5, Table S10). The initial rise in Ca$^{2+}$ concentrations at all depths could be due to upwelling of higher TDS from deeper groundwater, possibly sustained by the occurrence of calcite dissolution buffering pH-decreases caused by various processes discussed above. Throughout the experiment, Ca$^{2+}$ remained above baseline concentrations in groundwater at 2 m, 6 m and 8 m depths (Figure 5 and Table S10). Computed
saturation indices for groundwater from well M7 at depths of 2 m, 6 m, and 8 m demonstrate that groundwater remained near equilibrium with calcite throughout the experiment (Figure S9), confirming its reactivity and presence in the aquifer. Increases of Mg$^{2+}$ and Na$^+$ concentrations in groundwater may be due to upwelling of higher TDS groundwater from 8 m to 9 m depths in response to the natural gas injection and/or due to displacement from cation exchange sites by Ca$^{2+}$ stemming from calcite and/or dolomite (for Mg$^{2+}$) dissolution (Figure 5 and Table S10). The increase in H$_4$SiO$_4$ concentrations can be attributed to dissolution of silicate minerals (e.g. amphiboles, feldspars, chlorite are all present in the Borden aquifer) as a result of the mild pH decrease. Geochemical speciation calculations for groundwater from well M7 also indicated that groundwater was undersaturated with respect to gypsum, dolomite, pyrochroite, rhodochrosite and amorphous silica (Figure S9), implying that these phases do not act as solubility controls for Ca$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, and SO$_4^{2-}$ ions. In general, changes in major ions were minor (Table S10) and most concentrations were trending back to baseline levels towards the end of the experiment (day 700, except H$_4$SiO$_4$).

A primary concern regarding GM into groundwater is the mobilization of trace elements through biogeochemical reactions induced by fugitive CH$_4$ (Vidic et al., 2013). The extent of trace element mobilization is a function of local aquifer geochemistry and sediment mineralogy. Changes in trace element concentrations were minor, fluctuating above and below baseline levels throughout the experiment. Displacement of water from 8 m to 9 m depths due to the gas injection may have contributed to an increase in trace elements at 2 m and 6 m depths (Figure 7). An additional potential explanation for increased trace element concentrations is their release due to cation exchange and surface complexation reactions associated with increases in major ions. Most trace elements started to decrease post injection, except for Al, As, Zn, and Cr, which were
still above baseline on day 700 (Figure 7). Similar to H$_4$SiO$_4$, increased Al concentrations were likely caused by the dissolution of silicate minerals, but concentration increases were limited as indicated by undersaturated conditions with respect to amorphous aluminum hydroxide [Al(OH)$_3$(a)] (Figure S9). While various mechanisms likely contributed to the fluctuation in trace elements, the exact processes were difficult to discern amongst the natural variability observed in the aquifer. It is possible that fluctuations in groundwater temperature affected concentrations of dissolved ions. However, groundwater temperature in the Borden aquifer is relatively constant around 10 °C at depths between 5 m to 9 m bgs (Allen-King et al., 1995; Arildskov and Devlin, 2000; Nielsen et al., 1996), implying that variations in concentrations are unlikely due to seasonal effects.

Although not a major mechanism for CH$_4$(aq) oxidation, minor reductive dissolution of Fe and Mn-oxides did occur, as evidenced by the increase in Fe$^{2+}$ and Mn$^{2+}$ concentrations (Figure 4). Reductive dissolution reactions are well known to contribute to the release of trace elements due to the destruction of sorption sites (Appelo and Postma, 2004). In particular, mobilization of As poses major health risks even at low concentrations (EPA maximum contaminant level [MCL] is 0.13 μmol L$^{-1}$). On day 300 at 8 m depth, locations around the injection point (M5, M6, and M11) had groundwater with As concentrations above the EPA MCL, up to 0.20 μmol L$^{-1}$ (Table S11). Aside from the samples at 8 m depth on day 300, all other samples (including baseline, Table S9) had As concentrations below the MCL (Figure 7). Although changes to the aquifer geochemistry were minor throughout our experiment, short-term and long-term trends associated with the natural gas injection and CH$_4$(aq) oxidation, respectively, were evident.

3.5. Short and long-term biogeochemical evolution
We hypothesize that two biogeochemical stages progressively evolved as a consequence of the natural gas injection and subsequent $\text{CH}_4(\text{aq})$ oxidation. First, in the short-term (day 0 to 300) groundwater geochemistry changed predominantly due to upwelling of deeper landfill leachate water with free phase GM. Minor changes were also associated with the introduced $\text{CO}_2(\text{g})$ in the natural gas. Second, in the long-term (day 300 to 700) additional geochemical changes were observed in groundwater due to both aerobic and anaerobic ($\text{NO}_3^-$ and $\text{SO}_4^{2-}$ respiration) metabolisms at all depths (Figure 8).

Entrainment of deeper groundwater into shallower groundwater with subsequent mixing can be explained by buoyancy-driven vertical migration of injected natural gas, causing lateral and upward displacement of landfill leachate and groundwater around the injection zone (Figure 8a). The extent of this condition locally is masked by sampling scale/resolution. Enhanced mixing in groundwater has also been observed in air sparging studies due to the formation and collapse of gas channels during air injection (Heron et al., 2003; Kirtland and Aelion, 2000; Yang et al., 2005). A similar analogy can be made for our study where the formation and collapse of channels, as gas vented towards the atmosphere, created pathways for entrainment of deeper landfill impacted groundwater to migrate vertically and mix with shallower water (Figure 8a). The hydrogeochemical changes due to groundwater mixing were enhanced by disturbances from $\text{CO}_2(\text{g})$ dissolution.

In the long-term, $\text{CH}_4(\text{aq})$ oxidation progressed and, in some locations, approached completion between day 300 and 700, as evidenced by low residual concentrations and a strong $^{13}\text{C}$ enrichment in $\text{CH}_4$ (Figure 8b). However, geochemical impacts associated with $\text{CH}_4(\text{aq})$ were minor, limited by carbonate mineral dissolution. Arsenic was the only trace element that exceeded drinking water standards for a short time period 8 m bgs. Few studies have constrained
CH$_4$(aq) oxidation rates in the context of fugitive GM. In natural systems, CH$_4$(aq) oxidation rates (both aerobic and anaerobic) can range widely from $10^{-2}$ to $10^{-8}$ g CH$_4$ L$^{-1}$ day$^{-1}$ (Roy et al., 2016). Higher oxidation rates require abundant presence of O$_2$(aq), which was not the case in our study. The long-term results (day 300 to 700) suggest that for this small volume release experiment, oxidation led to natural attenuation of CH$_4$(aq) but only subtle changes in aquifer geochemistry.

The assessment for fugitive CH$_4$ natural attenuation potential and magnitude of secondary groundwater impacts from degradation reactions remains an important topic of research. Previous field studies have demonstrated that fugitive CH$_4$ can persist in an aquifer for long periods of time (Schout et al., 2017; Wolfe and Wilkin, 2017). Schout et al. (2017) measured elevated CH$_4$(aq) concentrations in an aquifer 50 years after a gas well blowout occurred. While our results demonstrate that CH$_4$(aq) can be oxidized, they also suggest that the rate of oxidation in groundwater is low. These findings support previous studies that show CH$_4$ can persist if present as a free phase gas in high abundance (e.g. Schout et al., 2017) and under oxygen-limited conditions. Similar temporal scales have been reported for natural attenuation studies at organic and hydrocarbon contaminant release sites (Essaid et al., 2011; Scow and Hicks, 2005).

The rate and mechanism(s) of aquifer-specific fugitive CH$_4$ attenuation need to be constrained to characterize potential risks of GM. The hydrogeochemical impacts associated with fugitive gas invasion and CH$_4$ attenuation will further depend on the aquifer specific hydro-biogeochemistry, the magnitude and duration of gas leakage, and the composition of natural gas (i.e. CO$_2$(g) content). The mineralogy of the Borden aquifer allowed for sufficient buffering to minimize hydrogeochemical impacts. However, this may not be the case for other sedimentary
basins with oil and gas development. Limited impacts are also due to the relatively small volume of injected gas in comparison to reported well blowouts which saw impacts > 500 m from the well (Kelly et al., 1985; Schout et al., 2017) and over an 11 km² area (Kelly et al., 1985).

However, our controlled experiment demonstrated that hydro-biogeochemical changes due to fugitive GM can occur even on a small scale (aquifer volume and mass of gas released). The short- and long-term results emphasize the need for appropriate monitoring corroborated by site specific characterization involving: 1) aquifer hydro-biogeochemistry, lithology and mineralogy; 2) gas composition, rate of release and duration.

4. Conclusion

Simulated wellbore leakage through a natural gas injection led to vertical entrainment and mixing of deep, lower quality water with shallow, higher quality water within a surficial unconfined aquifer system. Upwelling of deep water transported major ions and trace elements into the shallower aquifer causing a deterioration in water chemistry. Geochemical changes in the groundwater were also caused by the addition of CO₂(g) (0.8 %) and to a much lesser degree O₂(g) (0.05 %) present in the simulated natural gas. Depending on the natural aquifer geochemistry, subsurface leakage of natural gas with elevated CO₂(g) contents could have significant effects to the water chemistry, in particular due to more pronounced pH decreases. Although minor, the dynamic changes in groundwater chemistry during active injection demonstrate the need to better characterize processes induced by free phase fugitive GM from oil and gas wells. There is a potential for deep water with high TDS (e.g. saline) to be displaced by free phase GM, impacting water chemistry in shallow aquifers.
Post injection (up to 700 days) CH$_4$(aq) persisted in groundwater, but stable carbon isotope ratios provided strong evidence for CH$_4$ attenuation by oxidation in parts of the aquifer. Microbial community profiling implied capacity for aerobic CH$_4$(aq) oxidation, concomitant with anaerobic respiration of nitrate and SO$_4^{2-}$, and to a lesser extent Fe-oxides. Although fugitive GM impacts are aquifer specific, long-term changes in the Borden aquifer did show slight increases in trace elements. Throughout the experiment, pH variations and associated geochemical changes were limited by carbonate mineral dissolution. To fully delineate groundwater risks from fugitive GM, the mechanism(s) and rates of natural CH$_4$ attenuation need to be better constrained. The simulated release of natural gas into a shallow unconfined aquifer led to a persistent CH$_4$ groundwater plume with minor changes in major ions and trace elements associated with the gas injection and CH$_4$(aq) oxidation. However, hydro-biogeochemical impacts from fugitive GM will be specific to the natural aquifer composition, baseline groundwater composition and the nature of the gas leakage.

**Acknowledgements**

This research was funded by an NSERC Strategic Partnerships Grant (SPG-P) Grant no. 463045-14 led by the University of Guelph. Further support through an NSERC Research Tools and Instrument (RTI) Grant and a CFI-LOF grant awarded to K.U. Mayer and a NSERC discovery grant to B. Mayer is gratefully acknowledged. We thank Michael Nightingale, Andreas Haggman, Bethany Ladd, Dylan Klazinga, Terri Cheung, Leon Halwa, and Alyssa Verdin for their field and laboratory assistance.
References


**Figure Captions**

Figure 1. A) Map of Canada with the location of Canadian Forces Base Borden in Ontario marked by a black dot. B) Monitoring network with multilevel wells (M1-M32) spanning 10 m down-gradient from the injection zone in the direction of groundwater flow. C) Cross-section along the injection line (A-A’) of the Borden aquifer depicting hydrogeochemical conditions and landfill leachate with sampling points and injection screens at depth.

Figure 2. Log-log plot of average dissolved gas concentrations in groundwater from all multilevel wells sampled on respective days. Concentrations are given in mmol L\(^{-1}\) at 2 m (red), 6 m (blue), and 8 m (black) for CH\(_4\)(aq), CO\(_2\)(aq), and N\(_2\)(aq) with time elapsed since injection. Baseline conditions are averaged from three sampling events (days -49, -21, and -2) and shown
as day 5. Maximum average concentrations for each depth and dissolved gas are marked with a black square. A dashed line from the baseline values is shown for each depth.

Figure 3. A) Stable carbon isotope ratios for CH$_4$ plotted versus CH$_4$(aq) concentrations (mmol L$^{-1}$) from day 300, 500, and 700 at 2 m to 8 m depth. Elevated $\delta^{13}$C-CH$_4$ values suggest the occurrence of CH$_4$(aq) oxidation, particularly on day 500 at 8 m and 2 m bgs. Fractionation associated with diffusive migration is most evident from $^{12}$C-enrichment at 2 m depth. B) Gas dryness (ratio of methane [C$_1$] to ethane [C$_2$] plus propane [C$_3$]) plotted versus $\delta^{13}$C-CH$_4$ values from day 300, 500, and 700 for groundwater from 2 m to 8 m depth. Some samples where $\delta^{13}$C-CH$_4$ > -20 ‰ did not have detectable C$_2$ and C$_3$ concentrations and are thus not included.

Figure 4. Log-log plot of average concentrations of redox indicator species in groundwater from all multilevel wells sampled on respective days. Concentrations are given in mmol L$^{-1}$ at depths of 2 m (red), 6 m (blue), and 8 m (black). Baseline conditions are averaged from three sampling events (days -49, -21, and -2) and shown as day 5. A dashed line from the baseline value is shown for each depth.

Figure 5. Log-log plot of average concentrations of major ions in groundwater from all multilevel wells sampled on respective days. Concentrations are given in mmol L$^{-1}$ at depths of 2 m (red), 6 m (blue), and 8 m (black). Baseline conditions are averaged from three sampling
events (days -49, -21, and -2) and shown as day 5. A dashed line from the baseline concentrations is shown for each depth.

Figure 6. A) Major ion composition for groundwater at baseline conditions and day 28. Groundwater composition changed on day 28 when EC increased above baseline. The composition at 2 m depth approached ratios similar to baseline conditions at 6 m depth. The composition at 6 m depth on day 28 was close to baseline groundwater from 8 m depth. B) Log-log plot of Cl versus SO$_4^{2-}$ concentrations (mmol L$^{-1}$) in groundwater at 2 m (blue), 6 m (green), and 8 m (purple) depths from before, during, and post injection. Mixing lines based on Phreeqc simulations for samples from 2 m and 6 m depths and, 6 m and 8 m depths indicate mixing trends of groundwater from these depths during injection.

Figure 7. Log-log plot of average concentrations of trace elements in groundwater from all multilevel wells sampled on respective days. Concentrations are given in μmol L$^{-1}$ at depths of 2 m (red), 6 m (blue), and 8 m (black). Baseline conditions are averaged from three sampling events (days -49, -21, and -2) and shown as day 5. A dashed line from the baseline concentrations is shown for each depth.

Figure 8. Conceptual model for the natural gas injection experiment. A) Active injection (day 0 to 72) led to an extensive free and dissolved phase CH$_4$ plume. Injection of free phase gas entrained groundwater from the landfill leachate plume at 9 m depth, leading to mixing with shallower water. B) Long-term (>300 days post injection) CH$_4$(aq) persisted in the aquifer with an increase in microbially mediated CH$_4$(aq) oxidation.
Figure 2
Figure 4
Figure 5
Figure 6
Figure 7