Three-dimensional numerical simulations of methane gas migration from decommissioned hydrocarbon production wells into shallow aquifers

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Abstract Three-dimensional numerical simulations are used to provide insight into the behavior of methane as it migrates from a leaky decommissioned hydrocarbon well into a shallow aquifer. The conceptual model includes gas-phase migration from a leaky well, dissolution into groundwater, advective-dispersive transport and biodegradation of the dissolved methane plume. Gas-phase migration is simulated using the DuMuX multiphase simulator, while transport and fate of the dissolved phase is simulated using the BIONAPL/3D reactive transport model. Methane behavior is simulated for two conceptual models: first in a shallow confined aquifer containing a decommissioned leaky well based on a monitored field site near Lindbergh, Alberta, Canada, and secondly on a representative unconfined aquifer based loosely on the Borde, Ontario, field site. The simulations show that the Lindbergh site confined aquifer data are generally consistent with a 2 year methane leak of 2–20 m3/d, assuming anaerobic (sulfate-reducing) methane oxidation and with maximum oxidation rates of 1 × 10−3 to 1 × 10−2 kg/m3/d. Under the highest oxidation rate, dissolved methane decreased from solubility (110 mg/L) to the threshold concentration of 10 mg/L within 5 years. In the unconfined case with the same leakage rate, including both aerobic and anaerobic methane oxidation, the methane plume was less extensive compared to the confined aquifer scenarios. Unconfined aquifers may therefore be less vulnerable to impacts from methane leaks along decommissioned wells. At other potential leakage sites, site-specific data on the natural background geochemistry would be necessary to make reliable predictions on the fate of methane in groundwater.

1. Introduction

Poor completion of hydrocarbon wells, including incomplete closure and abandonment, is a known problem in the oil and gas industry which can lead to “leaky wells” [Dusseault and Jackson, 2014]. The resulting leakage and upward migration of fluids from deep geological formations to the shallow subsurface over long time scales can contribute to groundwater contamination and greenhouse gas emissions. These fluids can include stray gases (primarily methane), and formation waters, usually originating from the production or intermediate zones, which can migrate to surface or the shallow subsurface via preferential pathways in the case of poorly cemented casings and/or improperly sealed decommissioned wells [Jackson et al., 2013a; Dusseault et al., 2014; Dusseault and Jackson, 2014; Nowamooz et al., 2015; Reagan et al., 2015]. In shale gas or related unconventional hydrocarbon source wells or indeed any well which needs to be hydraulically fractured, including some deep geothermal wells, leakage of fracture fluids is also a concern [DiGiulio et al., 2011], although conclusive cases of such leakage are limited.

Recent isotopic evidence shows that 75% of leaking gas observed from wells in western Canada originated from nonproductive geological formations within the intermediate zone which separates the production zone from shallow freshwater aquifers [Muehlenbachs, 2012; Jackson et al., 2013a; Canadian Council of Academies (CCA), 2014]. Because of high costs of monitoring and lack of interest in their unprofitable gas resources, these intermediate zones are often poorly characterized despite the availability of the needed technologies [Jackson et al., 2013a].

In western Canada, 7–19% of the production wells completed between 2005 and 2007 have been affected by gas migration along the casing annulus, 9–28% showed gas leakage through the surface casing [Bexte et al., 2008], while 15% of production wells drilled up to 1995 in the United States showed fluid leakage...
following primary cement completions (Dusterhoft et al. [2002] as referenced in Jackson et al. [2013a]). In particular, Erno and Schmitz [1996] observed these trends in the Lloydminster area in western Canada. According to the Canadian Council of Academies’ report on environmental risks of shale gas development [CCA, 2014], the engineering challenge of avoiding long-term gas leakage and of maintaining production well integrity is a primary concern of the industry which needs to be resolved.

In order for upward fluid migration to occur from a source zone, two conditions are required: (1) a pathway and (2) a driving force (high upward pressure gradient [Flewelling and Sharma, 2013]). With respect to pathways, the most probable pathway for fluid migration identified by the CCA [2014] is from the Intermediate Zone through existing micro fissures within the annulus along the production well. Using numerical simulations, Nowamooz et al. [2015] showed that poor cement quality can lead to preferential pathways and fluid and gas migration along decommissioned shale gas wells.

Recent field investigations have provided compelling evidence of borehole leakage. For example, Osborn et al. [2011] and Jackson et al. [2013b] highlighted an increase in methane concentration with respect to distance from shale gas production wells in north-eastern Pennsylvania and upstate New York (although Saba and Orzechowski [2011] suggested the Osborn et al. data were inconclusive). Furthermore, Sechman et al. [2013] found significant concentrations of light hydrocarbons, carbon dioxide and total dissolved solids (TDS) in the vicinity of three gas wells and suggested that improperly sealed production wells may significantly affect subsurface water quality. More recently, Hammond [2016] compiled and analyzed geochemical and geological data collected in the area around Dimock Township (north-eastern Pennsylvania) between 2009 and 2012 (following methane contamination of water wells in 2009) and provided a comprehensive interpretation of temporal and spatial variations in gas concentrations and associated isotopic signatures related to gas well activities in the studied area.

Indeed, migration of natural gas into shallow aquifers can have significant impacts on groundwater chemistry such as increasing pH and alkalinity, mobilization of Fe$^{2+}$, Mn$^{3+}$, Ca$^{2+}$ and sulfides, and decreasing concentrations of dissolved oxygen (DO), SO$_2^{2-}$ and NO$_2^-$ [Kelly et al., 1985]. Similarly, numerical simulations conducted by Schwartz [2014] involving a hypothetical leak of gas-phase methane into a Quaternary aquifer in Germany showed a decrease of oxygen fugacity and decreased As, Cd, Ni, Pb and U concentrations associated with an increase of pH and Se and Cr concentrations. As dissolved methane concentrations above solubility can result in explosion and asphyxia hazards [Vidic et al., 2013], the US Office of the Interior [Eltischlager et al., 2001] used a threshold of 10 mg/L to identify water supply wells at possible risk. In Canada, the risk limit varies by province; Quebec, for example has adopted 7 mg/L methane as the criterion for increased risk where follow-up would be required, and 28 mg/L at which some immediate action must be taken. Moritz et al. [2015], for example, present a background methane survey in southern Quebec and found primarily biogenic gas, with 18 wells out of 130 exceeding the 7 mg/L criterion. They found correlations with background chemistry and proximity to natural faults, and suggested that dispersion, migration and oxidation could have played a role in the observed concentrations.

As noted by Knittel and Boetius [2009], methane oxidation via microbial processes is a major actor in methane consumption that can occur in a wide variety of marine and terrestrial environments including groundwater systems. Microbial populations responsible for methane oxidation can use a variety of terminal electron acceptors (TEAs) depending on their availability and the energy yields of the reaction. Oxygen is generally first consumed followed by NO$_3^-$, Mn$^{4+}$, Mn$^{3+}$, Fe$^{3+}$ and SO$_4^{2-}$ [Appelo and Postma, 2005]. Amos et al. [2011], for example, found evidence of aerobic methane oxidation through high oxygen recharge water in a petroleum contaminated aquifer near Bemidji, Minnesota.

Although numerous studies have shown that aerobic methane oxidation can be effective in terrestrial environments where oxygen is the preferred electron acceptor used by microorganisms, few have considered anaerobic methane oxidation in shallow aquifers. Grossman et al. [2002] observed anaerobic oxidation in a landfill leachate plume in Oklahoma and showed that this process is effective for reducing methane concentrations in contaminated aquifers. Furthermore, Van Stempvoort et al. [2005] found geochemical evidence of coupled methane oxidation and bacterial sulfate reduction following gas-phase methane migration from a leaky abandoned oil production well into a confined aquifer in western Canada (on which our Conceptual Model 1 is based). A more recent experimental study conducted by Berta et al. [2015], however, suggests that no short-term anaerobic methane oxidation would be expected in some shallow...
Aquifers following a CH₄ leak because of the slow growth rate of the microbial population. Their conclusions were based on lab column experiments and relatively low concentrations of methane and background sulfate.

Although most studies suggest anaerobic oxidation could be an efficient process to mitigate dissolved methane, it can also produce contaminant by-products such as HS⁻ which is associated with hydrogen sulfide (H₂S) in groundwater [Appelo and Postma, 2005]. The presence of H₂S in drinking water (which has a solubility of 5300 mg/L at atmospheric pressure and 10°C [Weil et al., 2006]) is generally associated with a strong and unpleasant rotten egg odour and an unpleasant taste even at very low concentrations. Furthermore, H₂S is recognized as an extremely flammable, highly toxic and eye-irritant gas. Consequently, a threshold of 0.05 mg/L of H₂S(aq) has been proposed by Health Canada to identify excess levels of hydrogen sulfide in drinking water [Health Canada, 1992].

Although fluid migration along production wells was identified in the CCA [2014] report as one of the major causes of groundwater contamination linked with oil and gas field operations, very few studies have addressed the efficiency of natural attenuation processes to restrict dissolved natural gas concentrations in contaminated aquifers. This is particularly difficult to assess considering the site-specific chemical and physical characteristics. In this context, numerical simulations can help to understand and evaluate long-term impacts of fluid migration along production wells and to assess the natural mitigation capacity of shallow aquifers.

In the current study, three-dimensional numerical simulations using the DuMu* multiphase simulator coupled to the reactive transport model BIONAPL/3D were first completed based on a real confined aquifer (Scenario 1) which had become contaminated by methane from a leaky well (known as the “Lindbergh site” [Van Stempvoort and Jaworski, 1995; Van Stempvoort et al., 1996; Maathuis and Jaworski, 1997; Van Stempvoort et al., 2005]). In Scenario 2, the models are applied to a hypothetical unconfined shallow aquifer, based loosely on the Borden, Ontario, well-characterized aquifer, but using the same leaky well scenario parameters as in the Lindbergh site. In both scenarios, bacterial-driven methane degradation processes were also included to evaluate the potential for natural mitigation of dissolved methane under different background chemistry and groundwater velocities. In the Lindbergh confined aquifer scenario (Scenario 1), sulfate was considered as the only electron acceptor, while both oxygen and sulfate were considered in the unconfined aquifer scenario (Scenario 2). Production of sulfide (HS⁻) as a by-product of anaerobic methane oxidation was included in both scenarios. The main objectives were to gain insight into the behavior of methane in shallow aquifers and to assess the effect of leakage duration and magnitude of the gas inflow rate as well as biodegradation processes on dissolved methane concentrations.

We first introduce the Lindbergh site as motivation and a field control for developing the numerical model, then present the common numerical simulation approach applied to both the Lindbergh confined aquifer (Scenario 1) and to the unconfined hypothetical case (Scenario 2). Details on the conceptual model for Scenario 1 are then provided, and the corresponding simulation results are presented and discussed. The Scenario 2 conceptual model (for an unconfined aquifer) is then defined and the simulations presented. The paper concludes with a discussion and comparison of results.

2. Lindbergh Site Context and Hydrogeology

The confined aquifer case (Scenario 1) is based on a research site located in the vicinity of Lloydminster, close to the Alberta – Saskatchewan border in Canada [Van Stempvoort et al., 2005], and which contained a deep oil production well. As outlined by Van Stempvoort and Jaworski [1995], the production well was drilled by Amoco Canada in December 1983, and exploited from February 1984 to November 1987. The well is 640 m deep and crosses the oil producing zone from 510 to 580 m below ground surface. A cemented surface casing was also installed which extends 100 m below ground surface (although no data are available on the cementing technique or cement quality). The corresponding borehole, surface casing and production casing diameters are 374, 273, and 177.8 mm, respectively. Oil was produced from the Lower Cretaceous Mannville Group consisting of interbedded sandstone, siltstone and shale that extends from 510 to 580 m below ground surface.

A test hole completed in May 1994 at the research site [Van Stempvoort and Jaworski 1995] showed the presence of a coarse-grained confined paleochannel as a part of the Empress Group extending from 25 to
50 m depth. Entirely pierced by the production well, this unit is mainly composed of medium to coarse sand and contains two horizons of gravel in the uppermost and lowermost 3 m. The underlying and overlying units are a marine clay/shale bedrock (the Lea Park Formation) and a clayey till, respectively.

Leaks were first noticed along the abandoned well in 1988 [Van Stempvoort et al., 2005]. According to Van Stempvoort et al. [1996], the gas source appeared to be the Cretaceous Mannville Group and/or underlying shale units such as the Lea Park Formation. No information was available regarding the duration or the magnitude of the leak, nor on the existence of any historical remedial activities to seal-off the gas migration (such as cement squeezing). In order to evaluate the impacts of natural gas leakage on the shallow confined aquifer, eight monitoring wells were installed at the site from 1994 to 2002. Water level measurements showed that the groundwater flow was toward the south-west, under a relatively low hydraulic gradient of $5 \times 10^{-5}$.

Sampling within 10 m of the production well between 1994 and 1996 indicated elevated methane concentrations with a thermogenic isotopic signature, and were associated with significant ethane levels. Also, decreasing sulfate concentrations associated with increasing Fe$^{2+}$ concentrations toward the top of the aquifer close to the production well suggested that both SO$_4^{2-}$ and Fe$^{3+}$ were being used as electron acceptors by microbial populations to oxidize methane [Van Stempvoort et al., 1996]. Background methane, iron, sulfate, bicarbonate and sulfide concentrations were measured at monitoring wells situated more than 50 m from the production well. Moreover, data from 2002 provided by Van Stempvoort et al. [2005] showed a strong decrease of both methane and sulfate concentrations within 10 m of the production well. However, iron concentrations did not show any decrease suggesting that sulfate had rapidly replaced Fe$^{3+}$ as the main electron acceptor. These data provided strong evidence that anaerobic methane oxidation linked with microbial sulfate reduction was occurring in the aquifer, especially toward the top of the aquifer just below the confining layer, following equation (1):

$$\text{CH}_4(\text{aq}) + \text{SO}_4^{2-} \rightarrow \text{HS}^- + \text{HCO}_3^- + \text{H}_2\text{O} \quad (1)$$

This observation was strongly corroborated by the isotopic composition of methane, sulfate and bicarbonate, and thus the above-mentioned authors proposed that anaerobic methane oxidation was effective near the production well.

Although methane oxidation linked with sulfate reduction is known to produce HS$^-$ via equation (1), Van Stempvoort et al. [2005] did not find increasing HS$^-$ concentrations close to the production well, as was expected. Instead, they suggested that HS$^-$ had possibly reacted with Fe$^{2+}$ or other metals, precipitating as sulfides, as reductive conditions predominated in the aquifer. Formation of zero-valent sulfur is also possible under reducing conditions [Milucka et al., 2012].

3. Numerical Modeling Approach

Multiphase flow (gas and water), and methane transport from a leaky well, was simulated in each scenario using the multiphase and multicomponent open-source DUNE module DuMux [Flemisch et al., 2011]. Since reactive processes are not available in DuMux, the simulated methane gas saturations were coupled (at each time step) to the BIONAPL/3D finite element model [Molson and Frind, 2015] for reactive transport of the dissolved gas phase.

Full details on the multiphase and multicomponent numerical simulations which were used to generate the well bore fluid leakages (i.e., methane and brine) used in the current paper can be found in Nowamooz et al. [2015], who evaluated methane and brine leakage along the cemented casing of a conceptual decommissioned shale gas well in the St Lawrence Lowlands (Québec, Canada). Their results showed that a properly cemented decommissioned well can prevent gas migration over a long time scale. However, a poorly cemented borehole resulted in gas leakage rates ranging from 0.04 m$^3$/d to more than 100 m$^3$/d, which corresponded well with surface casing vent flows measured on hydrocarbon wells elsewhere in Canada [Erno and Schmitz, 1996; Dusseault et al., 2014; Nowamooz et al., 2015].

The gas-phase leakage rates simulated by the DuMux model were then coupled to the BIONAPL/3D model which accounts for multicomponent advective-dispersive transport coupled with electron-acceptor limited biodegradation. An indirect coupling approach was adopted in which each model was run separately. In the DuMux model, simulated nodal gas-phase saturations throughout the aquifer were stored every day.
during the first year, and every month thereafter, to be later imported into the BIONAPL simulator. Within each time step in the BIONAPL model, gas dissolution into the flowing groundwater was assumed to occur at equilibrium (i.e., at methane solubility—see Conceptual Model 1 below—using existing model functionality for dissolving nonaqueous phase liquids (NAPLs)), and gas phase saturations were simultaneously updated to account for the mass loss to the water. Differences in time steps between the two models were accounted for by interpolating the bounding saturations. The approach reasonably assumes that within each time step, at the local scale around the well, the methane gas flux and dissolution into the water is much faster than dispersion and degradation of the dissolved methane.

The simulations were run for gas inflow rates varying from $2 \times 10^{-2}$ to $20$ m$^3$/d and leakage durations from 0.5 to 10 years (note that because of the domain half-symmetry, these total rates were divided by 2 when entered in the model).

Transport of the dissolved phase methane in BIONAPL/3D is governed by advection-dispersion following equation (2):

$$RiC = -D_{ij} \frac{\partial C}{\partial x_j} - q_i \frac{\partial C}{\partial x_i} + \frac{\partial}{\partial x_i} (C_i - C) - \omega \frac{\partial}{\partial x_i} \omega C$$

where $C$ is the dissolved methane concentration [kg/m$^3$], $R$ is the retardation factor [-], $\theta$ is the porosity [-], $S_w$ is the water saturation [-], $D_{ij}$ is the hydrodynamic dispersion tensor [m$^2$/s], $q_i$ is the Darcy flux [m/s], $C_i$ is the effective solubility of methane in water [kg/m$^3$], $\omega$ is the effective rate of methane gas phase dissolution in water [s$^{-1}$], $k_{BIO}$ is the effective biodegradation rate of methane [kg$_{methane}$/kg$_{microbe}$/s], $x_i$ are the spatial coordinates (x,y,z) [m], and $t$ is time [s].

The dissolution source term in equation (2) (the third term on the right-hand-side), normally applied for dissolution of a non–aqueous phase liquid [Frind et al., 1999], is adapted here to simulate the dissolution of the methane gas phase (provided by the DuMu$^4$ model) into the flowing water. A sufficiently high methane dissolution rate $\omega$ was enforced in the model to ensure methane solubility in water was reached under the given aquifer conditions.

We assume that methane oxidation coupled with oxygen and sulfate reduction follows a dual-Monod type kinetic model [Molson and Frind, 2015] given by equations (3–5) respectively:

$$\omega_{BIO}^{CH_4} = \sum_{n=1}^{A_n} k_{CH_4,n} M^n \left( \frac{1}{K_{CH_4,n} + C} \right) \cdot \frac{A^n}{K_{CH_4,n} + C} \cdot p^n$$

$$\omega_{BIO}^{O_2} = k_{CH_4,O_2} M^{CH_4} X^{CH_4,O_2} \left( \frac{C}{K_{CH_4,O_2} + C} \right) \cdot \left( \frac{1}{K_{CH_4,O_2} + A^{O_2}} \right) \cdot \rho^{O_2}_n$$

$$\omega_{BIO}^{SO_4} = k_{CH_4,SO_4} M^{CH_4} X^{CH_4,SO_4} \left( \frac{C}{K_{CH_4,SO_4} + C} \right) \cdot \left( \frac{1}{K_{CH_4,SO_4} + A^{SO_4}} \right) \cdot \rho^{SO_4}_n$$

where $\omega_{BIO}^{CH_4}$ and $\omega_{BIO}^{SO_4}$ are the effective oxygen and sulfate consumption rates, respectively, $[kg_{sulfate}/kg_{microbe}/d]$, $A^n$ is the concentration of the electron acceptor $n$ ($A^{O_2}, A^{SO_4}$) [kg/m$^3$], $M^n$ is the microbial concentration associated with electron acceptor $n$ ($M^{O_2}, M^{SO_4}$) [kg/m$^3$], $X^{CH_4,O_2}$ and $X^{CH_4,SO_4}$ are the stoichiometric mass ratios of EA consumption to methane consumption (kg$_{EA}$/kg$_{CH_4}$). $K_{CH_4,n}$ is the maximum oxidation rate of methane with electron acceptor $n$ ($k_{CH_4,n}$, $k_{CH_4,SO_4}$) [kg$_{methane}$/kg$_{microbe}$/d]. $N_A$ is the number of electron acceptors (here $N_A = 2$ : $O_2$ and $SO_4$).

The transport module in BIONAPL/3D is coupled to a 3D transient nonlinear groundwater flow equation which accounts for saturation-dependent relative permeability following the Corey [1987] function, in this case due to methane gas occupying the pore space around the leaky well. The flow-transport coupling and nonlinear relative permeability, dissolution and decay terms are handled using a Picard iterative scheme with central time-weighting. Deformable brick elements are used with an iterative watertable search for the unconfined aquifer scenarios, and both flow and transport matrices are solved using an efficient conjugate
Similar numerical approaches have been used in reactive transport modeling by Frind et al. [1999] and Molson et al. [2008, 2012].

4. Conceptual Model 1: The Lindbergh Site, Alberta, Confined Shallow Aquifer

The first conceptual model is based on the Lindbergh field site described by Van Stempvoort et al. [2005], in which a homogeneous, isotropic and confined aquifer of constant thickness is intersected by an abandoned vertical hydrocarbon production well (Figure 1). Composition of the gas phase migrating along the production well at the Lindbergh site was described by Van Stempvoort and Jaworski [1995], Van Stempvoort et al. [1996], Maathuis and Jaworski [1997] and Rich [1995] who identified methane as the main component although other hydrocarbons such as ethane and propane were also detected. Thus, gas entering at the base of the initially water-saturated aquifer was assumed to be only CH₄ and the presence of other thermogenic gases such as ethane and propane was neglected.

Based on simulation results obtained by Nowamooz et al. [2015], we used representative gas leakage rates into the base of the aquifer ranging from 0.02 to 20 m³/d for all subsequent simulations. These rates are considered reasonable because as mentioned by Nowamooz et al. [2015], most surface casing vent flows measured elsewhere in Canada fall within this range of magnitude despite the site-specific geological characteristics [Erno and Schmitz, 1996; Dusseault et al., 2014].

We implicitly assume that because of strong gas buoyancy and relatively low hydraulic gradients, the measured range of SCVFs, which are measured at ground surface, also reflects leakage rates entering the base of the aquifer. Gas phase migration along the borehole simulated with the DuMu'x code by Nowamooz et al. [2015] accounted for capillary pressure effects. Due to its likely negligible influence within the coarse-grained aquifers considered here, and to simplify the numerical procedure, the capillary pressure was set to zero in the current simulations. The effect of irreducible liquid and residual gas saturations on the numerical results is beyond the scope of this paper and will not be discussed here. As a first approach, gas entering the aquifer along the well annulus was assumed to flow constantly with time and was stopped abruptly after a given period. Thus our simulations account for the faulty cement seal indirectly through the applied leakage fluxes. All characteristics of the leakage scenarios which produced the given methane fluxes (including the cement permeabilities) are given in Nowamooz et al. [2015].

Figure 1. Conceptual model of methane leakage in the confined scenario, showing a confined shallow aquifer pierced by a vertical production or abandoned well that is leaking methane gas phase.
Methane solubility was calculated for the governing physical and chemical conditions at the top of the aquifer where most of the gas would accumulate. Assuming that methane and water are at equilibrium, methane solubility in water can be calculated using Henry’s law, given as:

\[ S_{CH_4} = p_{CH_4} \times k_H \]  

(6)

where \( S_{CH_4} \) and \( p_{CH_4} \) are the solubility and the partial pressure of methane, respectively, and \( k_H \) is the Henry coefficient of methane at temperature \( T \). Also, the partial pressure of methane can be calculated from Raoult’s law:

\[ p_{CH_4} = x_{CH_4} \times p_{tot} \]

(7)

where, neglecting the presence of other gases, \( p_{CH_4} = p_{tot} = 3.42 \text{ atm} \).

An appropriate Henry coefficient is calculated using the Van’t Hoff equation:

\[ k_H(T) = k_H(T^*) \cdot \exp \left( \frac{-\Delta H_{\text{solution}}}{R} \cdot \left( \frac{1}{T} - \frac{1}{T^*} \right) \right) \]

(8)

where \( k_H(T) \) is the Henry coefficient at the given temperature \( T \), \( k_H(T^*) \) is the Henry coefficient at the standard temperature \( T^* \) of 298.15 K (25°C), \( \Delta H_{\text{solution}} \) is the enthalpy of solution and \( R \) is the gas constant. Thus, considering \( k_H(T^*) = 1.3 \times 10^{-3} \text{ M/atm} \), a uniform temperature \( T \) of 278.15 K (5°C) and \(-\Delta H_{\text{gas}} = 1800 \text{ K [Sander, 1999]}\), the corresponding Henry coefficient can be given as \( k_H(T) = 1.98 \times 10^{-3} \text{ M/atm} \).

Introducing the calculated \( p_{CH_4} \) and \( k_H(T) \) in equation (6) and using a molar mass for methane of 16.04 g/mol, the CH\(_4\) solubility in water (\( S_{CH_4} \)) at the corresponding temperature, pressure and salinity conditions is approximately 110 mg/L. This value is consistent with the calculated methane solubility derived from Duan and Mao [2006].

Based on the relatively low solubility of methane at the corresponding physical and chemical conditions, the mass input of dissolved methane in the aquifer through brine migration was assumed to be negligible in comparison to the gas phase (consistent with Nowamooz et al. [2015] and Reagan et al. [2015]). Furthermore, any pressure disturbance caused by the brine influx was assumed to be too small to disrupt the natural hydraulic gradient. Also, the glacial till unit above the aquifer was assumed to be impermeable to water and gas thus preventing upward gas migration beyond the aquifer.

If the dissolved methane concentration exceeds its solubility, a methane gas phase is generated. Due to its low density, the gas-phase will migrate upward by buoyancy and will accumulate at the impermeable upper boundary of the confined aquifer. As the methane gas phase gradually dissolves into the groundwater, a dissolved methane plume will develop which is progressively transported by groundwater flow via advection and hydrodynamic dispersion. Methane dissolution into groundwater was assumed to be at equilibrium and will thus dissolve into the groundwater at its solubility concentration of 110 mg/L under the Lindbergh site conditions, which include a low groundwater flow rate. In the reactive scenarios, methane consumption was presumed to not affect the magnitude of the gas phase dissolution rate.

At the Lindbergh site, Van Stempvoort et al. [2005] proposed that the sulfate-reduction reaction given in equation (1) was effective for degrading dissolved methane close to the production well. Anaerobic oxidation was thus assumed to be the main process responsible for methane biodegradation, while methane oxidation through iron reduction was not considered. Although many studies have focussed on the anaerobic reaction rate of equation (1) in marine sediments, only limited data are available on anaerobic rates in shallow aquifers. As claimed by Knittel and Boetius [2009], the reaction rate depends mostly on methane and sulfate concentrations.

In the current study, existing data published in the literature will be used to infer a representative range of maximum oxidation rates based on methane and sulfate concentrations (Table 1). Based on the calculated methane solubility, a sulfate concentration of 400 mg/L [Van Stempvoort and Jaworski, 1995, Van Stempvoort et al., 1996, Maathuis and Jaworski, 1997; Van Stempvoort et al., 2005] and values from Table 1, maximum oxidation rates ranging from \( 10^{-5} \) to \( 10^{-3} \text{ kg/m}^2/\text{d} \) were considered representative for the Lindbergh site. These oxidation rates were then converted to \( \text{kg}_{\text{methane}}/\text{kg}_{\text{microbe}}/\text{d} \) \( (k_{CH_4}^{V_{\text{tot}}}) \) in equation (3)) to obtain the effective reaction rate \( k_{CH_4}^{V_{\text{tot}}} \) used in the BIONAPL/3D simulator. This conversion was made by dividing the corresponding oxidation rates derived from Table 1 by the background microbial population concentration given below.

For simplicity, processes able to mitigate sulfide concentrations such as sulfide mineral precipitation due to reducing conditions were not considered and thus the simulations can be considered a conservative or worst-case scenario with respect to HS\(^-\) concentrations.
Iversen et al.

Grossman et al.

Kosiur and Warford

Hoehler et al.

Bussman et al.

Treude et al.

Iversen and Jørgensen

Hansen et al.

Devol et al.

Reeburgh

Oxidation

Maximum oxidation rates were converted to \( \text{kg methane/kg microbe/d} \) as required in the BIONAPL/3D model. (N.D., not documented).

Table 2 summarizes the physical and chemical parameters used in the model for the confined case. While field-measured values for the hydraulic conductivity, porosity and background hydraulic gradient were used in the model, dispersivities were estimated based on the corresponding domain scale, following Schulze-Makuch [2005]. Finally, the CH₄ diffusion coefficient in the porous medium was determined at the above-mentioned conditions of pressure, temperature and salinity.

Methane consumption rate parameters for equation (1) were based on previous studies, assuming a background microbial concentration of \( 3 \times 10^{-5} \text{ kg/m}^3 \), half-utilization constants \( K_{\text{CH}_4, \text{SO}_4} \) and \( K_{\text{CH}_4, \text{S}^{2-}} \) of 0.055 and 0.2 kg/m³ for methane and sulfate, respectively (one-half their maximum concentrations), and a microbial yield coefficient of 0.03 for the microbe population involved in equation (1) [Schirmer et al., 2000; Knittel and Boetius, 2009]. A stoichiometric mass ratio of 6 kg sulfate/kg methane was also considered for equation (1) (represented by \( X_{\text{CH}_4, \text{SO}_4} \) in equation (5)). Finally, a representative range of maximum oxidation rates varying from \( 10^{-5} \) to \( 10^{-3} \text{ kg/m}^3/\text{d} \) was used in the following reactive simulations. The characteristics of all simulated cases for Scenario 1 and 2 are provided in Table 3.

Table 2. Physical and Chemical Parameters Used in the Numerical Simulations of the Confined (Scenario 1) and Unconfined (Scenario 2) Aquifer Scenarios

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Confined Aquifer (Scenario 1)</th>
<th>Unconfined Aquifer (Scenario 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic conductivity</td>
<td>( 6 \times 10^{-5} \text{ m/s} )</td>
<td>( 7.5 \times 10^{-3} \text{ m/s} )</td>
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<td>Porosity</td>
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<td>0.30</td>
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<td>Recharge rate</td>
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<td>180 mm/yr</td>
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<tr>
<td>Hydraulic gradient</td>
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<td>( 3.4 \times 10^{-3} \text{ m/s} )</td>
</tr>
<tr>
<td>Longitudinal dispersivity (( \xi_l ))</td>
<td>5 m</td>
<td>5 m</td>
</tr>
<tr>
<td>Transverse horizontal dispersivity (( \xi_{tr} ))</td>
<td>2.5 m</td>
<td>2.5 m</td>
</tr>
<tr>
<td>Transverse vertical dispersivity (( \xi_{tv} ))</td>
<td>0.01 m</td>
<td>0.01 m</td>
</tr>
<tr>
<td>CH₄ diffusion coeff in porous medium(^*)</td>
<td>( 10^{-3} \text{ m}^2/\text{s} )</td>
<td>( 10^{-1} \text{ m}^2/\text{s} )</td>
</tr>
<tr>
<td>CH₄ retardation factor</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^*\)Source: [http://visumod.freeshell.org/thermo/difcoef.html](http://visumod.freeshell.org/thermo/difcoef.html).

5. Domain Discretization, Boundary Conditions and Leakage Rates

In the confined aquifer scenario (as in the unconfined scenario), we take advantage of system symmetry about the vertical plane through the leaky well along the groundwater flow direction. Thus only one-half of the aquifer was simulated, with the flow system oriented parallel to the symmetry plane.

5.1. Domain Discretization

The model half-domain is 250 m \( \times 100 \text{ m} \times 25 \text{ m} \) in the \( x, y \) and \( z \) dimensions, respectively, and is completely pierced by a production well that is 0.2 m in diameter. The three-dimensional structured grid consists of 141 \( \times 63 \times 23 \) (= 204309) elements in the respective directions with a finer discretization close to the production well, at the top of the aquifer where most of the methane would be concentrated, as well as around the leakage point to account for a higher pressure gradient. Time steps varied from 0.01 to 1 day.

5.2. Boundary and Initial Conditions

In the DuMu\(^*\) multiphase model, the domain was assumed to be initially water-saturated. Fixed water pressures on the left (upgradient) and right (downgradient) faces of the domain (\( P_l \) and \( P_r \) in Figure 1), were used to impose a horizontal flow gradient of \( 5 \times 10^{-5} \text{ over the entire domain to enforce a uniform horizontal groundwater flow} \).
rates were applied in the DuMux model at the base of the aquifer at the production well over a 2 year period for the base-case simulations of each scenario. Indeed, Case 8a (Table 3), which accounts for advective-dispersive transport with consumption of methane through equation (1), will be used to show that a leakage duration of 2 years could reasonably reproduce the trend of dissolved methane measured at the Lindbergh site from 1994 to 2002 [Roy, 2016]. As no information concerning the duration of the gas leakage was available, methane migration along the production well was assumed to start in 1988, after the cessation of oil extraction activities. Thus, the year 1988 was set as time zero in the subsequent simulations. As detailed above, DuMuX simulations calculated transient gas-phase saturations were transferred to the BIONAPL/3D model as an internal source term.

### 6. Results and Discussion: Conceptual Model 1

#### 6.1. Cases 1–4: Nonreactive; Variable Gas Leakage Rate

Simulation results for the conservative (nonreactive) base-case scenario of the confined shallow aquifer assuming the two highest leakage rates of 2 m$^3$/d (Case 3) and 20 m$^3$/d (Case 4), respectively, are presented in Figure 2. The lower gas inflow rates ($2 \times 10^{-2}$ and $2 \times 10^{-1}$ m$^3$/d) did not produce a significant gas plume at the top of the aquifer and are presented in a complementary study [Roy, 2016]. In both leakage rate cases, the gas phase migrated upward along the production well by buoyancy and reached the top of the aquifer after approximately 4 days. A thin gas-phase plume accumulates at the top of the aquifer which spreads horizontally over time. The progressive dissolution of the methane gas phase creates a dissolved methane plume that also grows over time. An increase in the gas leakage rate of one order of magnitude resulted in a disc-shaped methane plume area approximately 3 times greater and heads at each end and no-flow boundary conditions on the remaining faces. The initial dissolved methane and sulfide (HS-) concentrations were set to 0 and 7 mg/L, respectively, throughout the domain. An initial background sulfate concentration of 400 mg/L was enforced for Case 7, 8, 9 and 11 (see Table 3), based on observed data at the Lindbergh site, using 40 mg/L for Case 10 representative of the Saint Lawrence Lowlands, Quebec, while a sulfate concentration of 40 mg/L was used for the remaining (nonreactive) simulations. A fixed sulfate concentration on the left (inflow) face (equal to background) and zero-gradient conditions for sulfate and methane were set on the remaining faces.

Impacts of gas migration were assessed through four gas inflow rates of 0.02, 0.2, 2, and 20 m$^3$/d covering the above-mentioned range of gas leakage rates simulated by Nowamooz et al. [2015]. These inflow rates were applied in the DuMuX model at the base of the aquifer at the production well over a 2 year period for the base-case simulations of each scenario. Indeed, Case 8a (Table 3), which accounts for advective-dispersive transport with consumption of methane through equation (1), will be used to show that a leakage duration of 2 years could reasonably reproduce the trend of dissolved methane measured at the Lindbergh site from 1994 to 2002 [Roy, 2016]. As no information concerning the duration of the gas leakage was available, methane migration along the production well was assumed to start in 1988, after the cessation of oil extraction activities. Thus, the year 1988 was set as time zero in the subsequent simulations. As detailed above, DuMuX-calculated transient gas-phase saturations were transferred to the BIONAPL/3D model as an internal source term.

### Table 3. Summary Characteristics of all 14 Simulation Cases, Identifying the Gas-Phase Methane Inflow Rate $Q$, Leakage Duration, Background Sulfate and Oxygen Concentrations and the Maximum Methane Oxidation Rates ($k_{CH,SO_4}$ and $k_{CH,O_2}$), Under Sulfate and Oxygen-Reducing Conditions, Respectively

<table>
<thead>
<tr>
<th>Case</th>
<th>$Q$ (m$^3$/d)</th>
<th>Leakage Duration (years)</th>
<th>$[SO_4]$ (mg/L)</th>
<th>$[O_2]$ (mg/L)</th>
<th>$k_{CH,SO_4}$ (kg/m$^3$/d)</th>
<th>$k_{CH,O_2}$ (kg/m$^3$/d)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>$2 \times 10^{-2}$</td>
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<td>0</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>2</td>
<td>$2 \times 10^{-1}$</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
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</tr>
<tr>
<td>7</td>
<td>2</td>
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<td>400</td>
<td>0</td>
<td>$1 \times 10^{-5}$</td>
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</tr>
<tr>
<td>8a</td>
<td>2</td>
<td>2</td>
<td>400</td>
<td>0</td>
<td>$5 \times 10^{-4}$</td>
<td>0</td>
</tr>
<tr>
<td>8b</td>
<td>2</td>
<td>2</td>
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<td>0</td>
<td>$1 \times 10^{-3}$</td>
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</tr>
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</tr>
<tr>
<td>10</td>
<td>2</td>
<td>2</td>
<td>40</td>
<td>0</td>
<td>$5 \times 10^{-5}$</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>2</td>
<td>400</td>
<td>0</td>
<td>$1 \times 10^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>12a</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>2-10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13a</td>
<td>2</td>
<td>2</td>
<td>30</td>
<td>2-10</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
<tr>
<td>14a</td>
<td>2</td>
<td>10</td>
<td>30</td>
<td>2-10</td>
<td>$1 \times 10^{-4}$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

*aCases 12--14 represent the unconfined aquifer which includes oxygen and sulfate (Scenario 2).
significantly thicker after 2 years. Due to the assumed slow background flow velocity, diffusion was the dominant transport process and thus only a limited downgradient migration of the dissolved methane pool from the leaky well could be observed. The 10 mg/L contour (corresponding to the threshold of methane concentrations used in the U.S.) reached a maximum distance of 63 and 104 m for Cases 3 and 4, respectively, after 2 years. The end of the gas leakage after 2 years produced a progressive decrease in the dissolved gas concentration but a peak methane concentration of 50 mg/L still remained in the aquifer after 5 years.

From the same nonreactive scenario (with no sulfate reduction), breakthrough (arrival) curves of dissolved methane concentrations for corresponding gas inflow rates ranging from 0.02 to 20 m$^3$/d are shown in Figure 3a at a monitoring well situated 5 m downgradient from the production well at the top of the aquifer. Methane, sulfate and sulfide concentrations measured by Van Stempvoort and Jaworski [1995], Van Stempvoort et al. [1996], Maathuis and Jaworski [1997] and Van Stempvoort et al. [2005] at a monitoring well at the top of the aquifer, and situated 5 m downgradient from the production well, are presented in Figures 3a–3e, for comparison purposes.

In response to gas arrival at the top of the domain, dissolved methane concentrations increased rapidly during the first few days in Case 2 (2 $\times$ 10$^{-1}$ m$^3$/d), 3 (2 m$^3$/d) and 4 (20 m$^3$/d), all reaching the methane solubility of 110 mg/L. The abrupt end of the gas leakage after 2 years was first accompanied by a rapid decrease of methane concentrations followed by significant tailing. For leakage rates above 0.2 m$^3$/d (Cases 3 and 4), concentrations still exceeded the threshold of 10 mg/L even after 25 years. In contrast, the methane concentration in Case 2 (2 $\times$ 10$^{-1}$ m$^3$/d) decreased below the threshold 17 years after the end of the gas leakage. The lowest gas inflow rate (Case 1, Figure 3a, 2 $\times$ 10$^{-2}$ m$^3$/d) resulted in a delayed arrival of the dissolved gas of approximately 1 year compared to other cases, clearly showing that the gas phase spread significantly less in this case. In contrast to other cases, the methane concentration reached the threshold approximately 5.5 years after the end of the gas leakage.

Figure 2. Simulated dissolved methane plume evolution from the nonreactive conservative base case scenarios (Cases 3 and 4), confined aquifer (Scenario 1), showing concentrations in the plan view at the top of the aquifer and in the vertical cross section through the leaky well at selected times over 10 years. Results represent gas leakages of 2 (left two columns) and 20 m$^3$/d (right two columns). The leakage ends after 2 years. The production well is illustrated by white circles in the plan views (not to scale).
6.2. Cases 5–6: Nonreactive; Variable Leakage Duration

As documented by Erno and Schmitz [1996], Dusseault et al. [2014], and Nowamooz et al. [2015], most leaky wells in western Canada have SCVFs ranging from 2 to 20 m$^3$/d. Thus, for all subsequent simulations of the nonreactive confined aquifer scenarios, we used a representative gas inflow rate of 2 m$^3$/d. Two additional conservative cases (Case 5 and 6) were then simulated using the 2 m$^3$/d gas inflow rate with leakage durations of 4 years and 6 months, respectively (Figure 3b). As expected, methane concentrations were higher with a longer exposure to methane leakage. In particular, Case 5 (4 year duration) did not meet the proposed threshold concentration within the 25 year simulation time frame. However, with the shortest duration (Case 6: 6 months duration), methane concentrations decreased to below the threshold concentration 19 years after the gas migration stopped.

6.3. Cases 7–9: Reactive; Sulfate Reduction (400 mg/L)

We also evaluated the effects on methane concentrations of the natural process of methane oxidation linked with sulfate reduction (equation (1)) using four different maximum methane oxidation rates of $10^{-5}$, $5 \times 10^{-5}$, $10^{-4}$, and $10^{-3}$ kg/m$^3$/d (Cases 7, 8a, 8b, 9, respectively) that cover the representative range of values inferred above. Dissolved methane concentrations as a function of time for Case 7, 8a, 8b and 9 are presented in Figure 3c. For Case 8a, we chose an oxidation rate that could best reproduce methane concentrations measured in the field whereas an intermediate oxidation rate was used in Case 8b. The representative gas leakage rate of 2 m$^3$/d was also used in these reactive simulations. Based on field measurements, initial background sulfate and sulfide concentrations of 400 and 7 mg/L, respectively, were enforced in the model. As expected, methane concentrations were very sensitive to the chosen maximum oxidation rate and decreased faster with time when a higher reaction rate was used. For example, in Case 7 ($10^{-5}$ kg/m$^3$/d),
Case 8b (10^{-4} \text{ kg/m}^3/\text{d}) and 9 (10^{-3} \text{ kg/m}^3/\text{d}), the threshold concentration of 10 mg/L was reached in the monitoring well 20, 4 and 2.5 years, respectively, after the end of the gas leakage. These simulation results also showed that the difference in methane concentrations between these cases became less important with increasing maximum oxidation rates, as sulfate availability became limiting. The reactive cases (Cases 7–9) were also generally consistent with the field data. In particular, Case 8a best reproduced the general trend marked by the observed methane concentrations [Roy, 2016].

Sulfate concentrations were also very sensitive to the maximum methane oxidation rate and a high oxidation rate was associated with a more rapid decrease in sulfate concentrations (Cases 7, 8b, 9; Figure 3d). In Case 9 (10^{-2} \text{ kg/m}^3/\text{d}), the high maximum oxidation rate resulted in a rapid consumption of sulfate concentrations that decreased below 5 mg/L only 1.5 years after the beginning of the gas leakage. In Cases 8b (10^{-4} \text{ kg/m}^3/\text{d}), and 9 (10^{-3} \text{ kg/m}^3/\text{d}), the sulfate concentrations tended to recover to their background levels once methane concentrations became negligible. As iron reduction linked with methane oxidation was not considered in the current model, none of the reactive simulations (even Case 8a) could exactly reproduce measured sulfate concentrations in the field. Indeed, as mentioned in Roy [2016], associated iron and methane consumption by microbial populations during the mid-1990s, would have slowed the decrease in sulfate concentrations.

As expected, the rate of sulfide (HS^{-}) production increased when using greater maximum methane oxidation rates (Figure 3e). Case 9 (10^{-3} \text{ kg/m}^3/\text{d}) showed a rapid increase in dissolved sulfide during the first year with concentrations peaking at about 142.5 mg/L after approximately 2 years (sulfide precipitation was not considered). Whereas methane and sulfate were rapidly consumed, production of sulfide declined and hydrodynamic dispersion caused HS^{-} concentrations to slowly decrease, reaching a concentration of 69 mg/L after 25 years. Case 8b (10^{-4} \text{ kg/m}^3/\text{d}) followed the same trend as Case 9 but with a smaller and delayed concentration peak reaching 83.6 mg/L after 6.5 years. This was related to the slower reaction rate in comparison with Case 9. A sulfide concentration of 46.5 mg/L remained at the end of the simulation. The low maximum oxidation rate used in Case 7 (10^{-5} \text{ kg/m}^3/\text{d}) resulted in a lower HS^{-} production compared to Case 8b and 9 and concentrations increased up to 28.4 mg/L at the end of the simulation. Thus, decreasing the maximum oxidation rate of methane also resulted in an increasing delay between peaks of sulfate concentrations. Finally, because sulfide precipitation as metal sulfide minerals was neglected in the current study, simulation results from Case 7, 8a, 8b and 9 tended to overestimate the dissolved sulfide measurement in 2002 [Van Stempvoort et al., 2005].

6.4. Case 10: Reactive; Sulfate Reduction (40 mg/L)

Aquifers situated in the prospective shale gas areas between Quebec City and Montreal in eastern Canada are characterized by natural background sulfate concentrations which are typically about 40 mg/L [Blanchette, 2006; Carrier et al., 2013; Larocque et al., 2013]. In order to evaluate impacts of gas migration on water resources in this particular area, we repeated the confined aquifer conceptual model simulation using this 40 mg/L value as a new initial sulfate concentration as well as a representative methane oxidation rate for the Lindbergh site of 5 \times 10^{-5} \text{ kg/m}^3/\text{d} and a gas inflow rate of 2 m^3/d (Figures 3c–3e—Case 10).

Simulation results for Case 10 showed that the methane concentrations did not decrease as much as in Case 8a which was characterized by the same oxidation rate but with a higher initial sulfate concentration of 400 mg/L (Figure 3c). Moreover, in Case 10, the methane concentrations did not reach the threshold criterion (10 mg/L) within 25 years. Sulfate was negligible after approximately 1 year (Figure 3d), which lead to the significant decrease in the methane consumption rate.

The production rate of sulfide was also affected by the rapid depletion in sulfate concentrations. The increase in HS^{-} was very similar for Case 8a and 10 during the first year since sulfate was still available in both cases (Figure 3e). Afterward, the rate of sulfide production decreased abruptly in response to the rapid sulfate depletion. Consequently, similar to Case 7 (10^{-5} \text{ kg/m}^3/\text{d}), HS^{-} concentrations did not reach a maximum.

6.5. Case 11: Reactive; Maximum Gas Inflow and Maximum Sulfate

A worse-case scenario representing high-contamination from sulfide was assessed in the final confined aquifer case using a maximum gas inflow rate of 20 m^3/d and a maximum methane oxidation rate of 10^{-3} \text{ kg/m}^3/\text{d} (Case 11). This maximum leakage rate was designed to produce a wide methane and sulfide plume
associated with high contaminant concentrations. Figure 4 presents plan views of the simulated dissolved methane and sulfide plumes and progression of the associated sulfate depletion zone for the base case from 1 to 10 years. During the first 2 years, the methane and sulfide plumes and the associated sulfate depletion zone spread widely over the domain and a maximum $\text{HS}^-\text{2}$ of 142.8 mg/L was reached close to the production well after 2 years. After 5 years, although the gas leakage had stopped and almost all the methane had been consumed, the dissolved sulfide plume continued to grow with time due to advection and hydrodynamic dispersion, while concentrations tended to decrease slowly to 142.2 mg/L close to the production well.

Similarly, the sulfate depletion zone in Case 11 expanded significantly while after the leak stopped (after 2 years), concentrations begin to recover by dispersion into the center of the plume since no methane remained in the aquifer. After 10 years, methane concentrations were below 10 mg/L throughout the domain while sulfate concentrations continued to increase slowly at the center of the depletion zone. Although the extent of the sulfate depletion zone did not increase laterally over the final 5 years, it tended to be thicker. With a relatively uniform thickness, the dissolved sulfide plume was approximately 100 m downgradient from the production well with most concentrated in the first 2 m at the top of the aquifer. Although $\text{HS}^-\text{2}$ concentrations continued to decrease afterward, they remained over 74.7 mg/L close to the production well after 10 years. Due to the low hydraulic gradient, and since $\text{HS}^-\text{2}$ was considered conservative (e.g., sulfide mineral precipitation was neglected), it would take several decades for $\text{HS}^-\text{2}$ to return to the background level of 7 mg/L. Although the maximum methane oxidation rate significantly affected the magnitude of the sulfide concentrations, simulation results showed that the gas inflow rate, as well as the leakage duration, were the main controls affecting the production of $\text{HS}^-\text{2}$.

6.6. High Groundwater Velocity

Impacts of a higher groundwater velocity on methane concentrations in the confined aquifer scenario were assessed by Roy [2016] using a higher hydraulic gradient of $5 \times 10^{-3}$ (corresponding to a groundwater velocity of 0.74 cm/d) and an average gas leakage rate of 2 m$^3$/d. An initial nonreactive simulation resulted in a narrow and elongated dissolved methane plume due to more rapid gas migration (not shown). Also, the decrease in methane concentrations following the end of the gas leakage was more significant compared to Case 3 (presented in this study) due to the higher flow velocity, reaching the 10 mg/L threshold concentration after 5 years. In the otherwise identical reactive case (with the higher velocity and with sulfate reduction assuming a maximum oxidation rate of $5 \times 10^{-5}$ kg/m$^3$/d), the differences in methane concentrations were small compared to the nonreactive case [Roy, 2016], with the threshold reached after 4 years.
7. Conceptual Model 2: Unconfined Shallow Aquifer

The conceptual model for methane gas- and aqueous-phase migration into a hypothetical shallow, homogeneous and isotropic unconfined aquifer is shown in Figure 5. The aquifer is assumed 25 m deep, which is pierced by a leaky decommissioned gas production well. Again, the relatively low methane solubility in water and the low leakage rate of brine along the well allows us to only consider the gas phase entering the aquifer while neglecting the mass flux of dissolved methane. An average constant gas leakage rate of 2 m$^3$/d [Erno and Schmitz, 1996; Dusseault et al., 2014; Nowamooz et al., 2015] was used which was assumed to end after a given period of time.

Methane solubility calculations used for the confined case were similarly applied here. As methane solubility tends to increase with depth, impacts of methane gas-phase migration are likely to be greater at the base of the unconfined aquifer. Thus, we conservatively assumed a uniform methane solubility of 110 mg/L as in the confined shallow aquifer case. Again, if the methane solubility is reached, a gas phase is created which tends to rapidly migrate upward along the production well and is progressively dissolving in groundwater. As no impermeable layer is present, the gas-phase should be free to leave the domain through the overlying unsaturated zone. Finally, capillary pressures were likewise set to zero.

Being exposed to the atmosphere, aerobic methane oxidation was added to the unconfined model following equation (9):

$$
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
$$

(9)

Since oxygen is the preferred electron acceptor, methane is assumed first consumed by oxygen (equation (9)) until oxygen is depleted. When anoxic conditions prevail, methane is consumed through sulfate reduction (equation (1)).

As with anaerobic methane oxidation (equation (1)) assumed in the confined aquifer scenarios (Lindbergh case), we assume that aerobic methane oxidation in the unconfined scenarios also follows dual-Monod type kinetics. Again, limited information is available concerning the kinetics of aerobic methane oxidation in groundwater thus representative maximum oxidation rates for the unconfined case ranging from $10^{-3}$ to $10^{-1}$ kg/m$^3$/d were chosen based on a compilation of values available for other environmental contexts (Table 4) and based on estimated methane and background oxygen concentrations. As required by the
BIONAPL/3D model, the maximum oxidation rates derived from Table 4 were converted to \([\text{kg methane/kg microbe/d}]\) by dividing the rates in Table 4 by the corresponding background microbial concentration given below.

A similar simulation strategy was used for the unconfined shallow aquifer case as applied in the real confined aquifer case in Alberta. Multiphase multicompontent simulations were run using the numerical model DuMu* and advective-dispersive reactive transport of dissolved methane and EA’s was simulated with BIONAPL/3D using equations (2–5).

In the unconfined scenario, the hydraulic gradient, porosity, hydraulic conductivity and recharge rate specific to the well-characterized Canadian Forces Base Borden site in Ontario (Canada) were adopted (Table 2). Values for the longitudinal, transverse horizontal and transverse vertical dispersivities, as well as the \(CH_4\) diffusion coefficient in water, were assumed identical to those used in the confined aquifer case.

The effective reaction rate for equation (9) was calculated by the BIONAPL3/D model assuming a range of maximum oxidation rates from \(10^{-2}\) to \(10^{-1}\) \(\text{kg/m}^3\text{d}\) (Table 4), an initial background microbial concentration of \(3 \times 10^{-3}\) \(\text{kg/m}^3\) and half-utilization constants of 0.055 and 0.001 \(\text{kg/m}^3\) for methane and oxygen, respectively (defined as one-half of their maximum concentrations), and a microbial yield coefficient of 0.5 [Schirmer et al., 2000]. Stoichiometric mass ratios of 6 \(\text{kg sulfate/kg methane}\) and 4 \(\text{kg oxygen/kg methane}\) were used for equations (1) and (9), respectively. As anaerobic methane oxidation (equation (1)) also applies in this unconfined shallow aquifer case, the same kinetic parameters from the confined case were used here. In the unconfined case, we also considered an electron acceptor inhibition constant of 0.001 \(\text{kg/m}^3\) [Molson and Frind, 2015] to use sulfate as the preferred electron acceptor only when oxygen is completely consumed through equation (9).

### 8. Domain Discretization, Boundary Conditions and Leakage Rates

#### 8.1. Domain Discretization

As the methane gas phase was expected to spread less laterally in the unconfined scenario, we used a symmetric half-domain of \(250\text{m} \times 50\text{m} \times 25\text{m}\) in the respective \(x, y\) and \(z\) directions (a vertical symmetry plane was again assumed through the leaky well), or half the width of the confined aquifer model, and discretized with \(141 \times 63 \times 33\) (= 223,344) elements.

#### 8.2. Boundary and Initial Conditions

Boundary conditions in the unconfined aquifer model were similar to those in the confined aquifer scenario, except for the top boundary and the imposed hydraulic gradient. In the DuMu* multiphase model, a ground surface recharge rate of \(5 \times 10^{-4}\) \(\text{m/d}\) (180 mm/yr) was imposed for the water phase to account for natural groundwater recharge. An initial hydraulic gradient of \(3.4 \times 10^{-3}\) was enforced across the model by applying fixed pressures \((P_L\text{ and } P_H\) in Figure 5) at the left (inflow) and right (outflow) faces to reproduce the groundwater velocity observed at the Borden site (\(\sim 7\) cm/d). No-flow boundary conditions were set on the remaining faces for the water phase.

For the gas phase, an outflow boundary condition was set on the top and right faces to allow gas to migrate upward and out of the domain while a fixed saturation was set on the left inflow face. A no-flow boundary condition for the gas phase was enforced on the other boundaries. Finally, a gas inflow rate of \(2\) \(\text{m}^3/\text{d}\) was set at the base of the aquifer at the location of the production well.

In the BIONAPL/3D model, the above-mentioned recharge rate carrying oxygen at a concentration of \(10\) mg/L was also imposed on the top face as a Type-3 (Cauchy) transport boundary. Methane, oxygen and sulfate concentrations equal to their respective background concentrations were fixed on the left inflow face and a zero concentration gradient boundary condition was imposed on the other faces. Initial concentrations for sulfate and sulfide were respectively set to 30 mg/L and 0 mg/L which correspond to the concentrations measured at the Borden field site [Nicholson et al., 1983]. Furthermore, we applied a linear oxygen concentration gradient over the entire thickness of the aquifer varying from 10 mg/L at the top of the aquifer to 2 mg/L at the bottom. The initial methane level was set to 0 mg/L. An initial transport simulation was first launched in order to obtain steady-state oxygen, sulfate and sulfide concentrations in the aquifer. These stable background conditions were then used as the initial condition in the subsequent
reactive transport simulations. Initial conditions used in the DuMu\textsuperscript{x} model were the same for the confined and unconfined case.

9. Results and Discussion: Conceptual Model 2


We evaluated the impacts of hypothetical gas migration into a shallow unconfined aquifer through three different cases (Case 12, 13 and 14) using a gas inflow rate of 2 m\textsuperscript{3}/d [Erno and Schmitz, 1996; Dusseault et al., 2014; Nowamooz et al., 2015] that stopped abruptly after a given period of time (2–10 years, see Table 3).

Simulation results in the vertical cross section parallel to groundwater flow for the unconfined case are presented in Figure 6, showing the evolution of methane, oxygen, sulfate and sulfide concentrations after 0, 1, 2, 5 and 10 years. The first row presents the assumed initial methane, oxygen, sulfate and sulfide concentrations in the aquifer. The methane gas phase migrated upward along the production well but did not spread further after 1 year, resulting in a much more limited horizontal extent of the methane impact area compared to the confined case. Moreover, while methane was migrating upward along the production well, it was progressively consumed through equation (9) resulting in a drop in oxygen concentrations over the entire thickness of the aquifer. The extent of the oxygen depletion zone was greater at the bottom of the domain due to the lower initial background oxygen concentrations and due to oxygen replenishment at the top from surface recharge.

The rapid drop of oxygen concentrations and low oxygen availability at the base of the aquifer lead to a rapid development of anoxic conditions, preventing further aerobic methane degradation. Sulfate reduction (equation (1)) then slowly begins to consume methane, resulting in a small sulfate depletion zone extending a few meters downdgradient from the production well. This depletion zone was already visible after 1 year as highlighted by the 30 mg/L contour in Figure 6. The resulting dissolved sulfide plume that overlaps the sulfate depletion zone extended approximately 135 m downdgradient from the production well and concentrations reached a maximum of 0.7 mg/L at the center of the plume after 1 year.

After 2 years, the leak was stopped, and the dissolved methane plume stopped spreading, thus limiting the methane contamination (thus the methane plume extent at 2 years in Figure 6 has already reached its approximate maximum extent). In response to the extension of the anoxic area, the sulfate depletion zone extended approximately 75 m downdgradient from the production well leading to an increase in length of the dissolved sulfide plume, reaching 70 m long. Also, the depletion zone spread over almost the entire thickness of the aquifer (from 0 to 20 m). Sulfide concentrations also increased at the center of the plume reaching 1.1 mg/L.
The end of the gas leakage at 2 years was followed by a progressive return to initial background concentrations for all components as shown in Figure 6 after 5 years. Whereas the dissolved sulfide plume was transported by groundwater flow up to 250 m downgradient, concentrations decreased significantly due to dispersion, and only 0.3 mg/L remained at the center of the plume after 5 years. Initial conditions prevailed for all components after 10 years.

Breakthrough (arrival) curves of methane, oxygen, sulfate and sulfide at an observation point 5 m downgradient from the production well, at the base of the unconfined aquifer, are shown in Figure 7. A conservative nonreactive simulation was first launched (Case 12) using a leakage duration of 2 years to determine the maximum methane concentrations for these specific conditions (Figure 7a). In this case, methane reached a sharp peak concentration of about 5.5 mg/L but did not reach the solubility of 110 mg/L since dissolved gas was rapidly flushed by the flowing groundwater. After 5 years, almost all the methane had disappeared.

Three values of the maximum oxidation rate of $10^{-3}$, $10^{-2}$ and $10^{-1}$ kg/m$^3$/d for equation (9) (aerobic methane oxidation) were then tested (Table 4) while a single intermediate reaction rate of $10^{-4}$ kg/m$^3$/d was chosen for sulfate reduction. Changing the maximum aerobic oxidation rate did not produce significant differences for methane, oxygen, sulfate and sulfide concentrations, thus only the intermediate reactive case involving a maximum reaction rate of $10^{-2}$ kg/m$^3$/d for equation (9) is presented in Figure 7, with a leakage duration of 2 years (Case 13).

Biodegradation significantly attenuated methane concentrations in this reactive case (Figure 7a). Indeed, methane only reached a maximum concentration of 3 mg/L at the end of the gas leakage. Methane concentrations then dropped rapidly and were negligible after approximately 2.5 years. As oxygen was the preferred electron acceptor used to consume methane, O$_2$ concentrations rapidly decreased during the first 50 days and anoxic conditions were maintained for about 2.5 years (Figure 7b). Following the end of the gas leakage, oxygen concentrations increased significantly and returned to their initial background level. In response to the development of anoxic conditions, the microbes progressively start to use sulfate as the main electron acceptor. As presented in Figure 7c, the drop in sulfate concentrations was very weak, only decreasing to a minimum of 27.9 mg/L. This leads to only a limited production of HS$^-$ which showed an increase of less than 1 mg/L after 2 years followed by a rapid decrease in response to natural attenuation (Figure 7d).

A worst-case scenario with respect to sulfide (Case 14) for the unconfined aquifer was then considered using a leakage duration of 10 years with a maximum oxidation rate of $10^{-1}$ kg/m$^3$/d for aerobic methane oxidation.
oxidation and the same anaerobic rate as in Case 13. In both Case 13 and 14, a maximum methane concentration of 3 mg/L was reached after 2 years and remained constant up to 10 years in Case 14 (Figure 7a), despite the longer leakage duration used. Also, methane consumption produced a significant anoxic zone surrounding the production well that lasted up to 10.5 years (Figure 7b).

Sulfate concentrations fell to a minimum of about 27.6 mg/L (Figure 7c) due to the longer exposure to gas-phase methane leakage. Both oxygen and sulfate concentrations tended to recover to their initial levels after the end of the gas leakage. Finally, sulfide concentrations increased up to 0.8 mg/L after 10 years, consistent with a longer duration of methane leakage (Figure 7d). Consequently, it appeared that a longer exposure of groundwater to gas leakage (Case 14) did not result in a significant drop of sulfate concentrations compared to Case 13. Moreover, the increase of sulfide concentrations was limited (Case 14 showed HS flux concentrations only 0.1 mg/L higher than Case 13) but the resulting plume spread over 150 m downgradient from the production well.

10. Conclusions

Three-dimensional numerical simulations were completed to assess the impact of methane gas- and dissolved-phase plume migration from a leaky hydrocarbon production well into a shallow aquifer. The conceptual models included natural-gradient groundwater flow, migration and dissolution of the gas-phase as well as advective-dispersive transport and biodegradation of the dissolved gas phase. The efficiency of bacterial-driven processes to mitigate methane concentrations was evaluated using different background geochemistry and inferred literature-based maximum oxidation rates. The conceptual models are nevertheless simplified, thus the results should be used only as an example. A full model calibration would be required for more detailed specific field sites.

Simulation results for the confined shallow aquifer case showed that the dissolved methane plume will likely concentrate at the top of the aquifer. The extent of the dissolved methane plume was mainly controlled by the magnitude of the gas leakage and the leakage duration. Maximum downgradient migration distances of 63 and 104 m were reached by the 10 mg/L contour in Case 3 and 4, respectively, after 2 years. Reactive simulations which included methane oxidation by sulfate reduction showed that methane concentrations were very sensitive to the maximum oxidation rate and that under suitable conditions (SO4 / C2H4 ≥ 10 mg/L, as observed at Lindbergh, and degradation rates ≥ 1 × 10^-3 kg/m^3/d), dissolved methane concentrations can be significantly attenuated by natural biodegradation.
In all confined aquifer simulation cases, methane concentrations rapidly exceeded the threshold concentration of 10 mg/L but dispersion and bacteriologically driven methane oxidation decreased concentrations to the threshold criterion after times varying from 4.5 years to more than 25 years. Two-year leaks at a rate of 2 m³/d, for example, were attenuated to below the 10 mg/L threshold, 20, 4 and 2.5 years after the end of the gas leakage under degradation rates of 10⁻⁵, 10⁻⁴ and 10⁻³ kg/m³/d, respectively. Although sulfate and sulfide concentrations were not accurately reproduced (in part because of a lack of data and high uncertainty), the trend marked by methane concentrations was best approximated by Case 8a (Roy, 2016). Notwithstanding the high uncertainty in the observed data, a better fit of the data regarding SO₄²⁻ and HS⁻ concentrations would require the consideration of methane oxidation linked with iron reduction that was suggested active at the Lindbergh site. Higher maximum oxidation rates supported production of sulfide, with a maximum HS⁻ concentration of 142.8 mg/L reached close to the production well in Case 11 which remained high (74 mg/L) even at the end of the 25 year simulation.

Simulation scenarios of leakage into an unconfined shallow aquifer, using physical and chemical parameters from the Borden site in Ontario, indicated that the methane gas-phase would remain principally along the production well but would not migrate significantly further, avoiding the development of a large impact zone such as in the confined shallow aquifer case. Unlike in the confined case, dissolved methane concentrations 5 m downgradient from the leaky well in the unconfined aquifer remained largely below the solubility limit and the threshold of 10 mg/L was never reached within the 25 year simulation time frame even for the nonreactive simulations. Reactive simulations showed that aerobic methane oxidation was able to rapidly consume methane. As oxygen was the preferred electron acceptor, the efficiency of anaerobic methane oxidation to mitigate methane concentration was less.

In the unconfined case the methane plume remained concentrated around the production well, while the oxygen and sulfate depletion zones, as well as the dissolved sulfide plumes, spread significantly downgradient in the aquifer. Groundwater sampling and water analysis for O₂, SO₄²⁻ and HS⁻, between 10 and 15 m downgradient from the production well, for example (as suggested in Case 13), could be used to monitor for any methane-oxidation induced drops in oxygen and sulfate concentrations, or for associated increases in sulfide concentrations. A similar approach would also be useful in confined aquifers, with monitoring wells focussed near the top of the aquifer.

In this context, the results suggest that unconfined aquifers may be less vulnerable to contamination from dissolved methane than confined aquifers. In the unconfined case, the gas-phase is free to escape into the overlying soils or atmosphere (which is nevertheless also a serious concern). Moreover, the unconfined aquifer case had lower concentrations of HS⁻ as methane consumption was dominated by aerobic methane oxidation, while sulfate reduction was much less.

In agreement with the CCA [2014] conclusions, this study suggests that the impact on groundwater resources due to gas migration from a leaky well will depend significantly on regional differences such as the hydrogeological context (hydraulic gradient, degree of confinement, etc.) as well as the background geochemistry, well density and well integrity. In particular, methane concentrations were very sensitive to the magnitude and duration of the gas leakage, the biodegradation rate and the background electron acceptor concentrations. Characterization of the natural background hydrogeochemistry combined with numerical simulations of the expected leakage scenarios is recommended to assess the ability of natural groundwater systems to attenuate dissolved methane from leaky wells.

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Acknowledgments
This research was supported by Environment and Climate Change Canada, by a Discovery Grant to the second author from the Natural Sciences and Engineering Research Council of Canada (NSERC), and by a Canada Research Chair in Quantitative Hydrogeology of Fractured Porous Media held by the second author. The authors wish to thank R. Lefebvre of the INRS, Quebec City, for useful discussions and Pierre Therrien of Universite Laval for his help with computational resources. Access to the public-domain DuMuX code is available at: http://www.dumux.org/. The BIONAPL/3D model is also freely available for research use. Please contact the corresponding author (john.molson@ggl.ulaval.ca) for inquiries related to the DuMuX model (including the adopted CH4/Brine fluid system) and the BIONAPL/3D simulation files used in this paper.


