MULTI-COMPONENT MASS TRANSFER OF BACKGROUND DISSOLVED GASES AND STRAY METHANE GAS IN SHALLOW GROUNDWATER SYSTEMS

by

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Abstract

The goal of this research was to investigate the effects of multi-component mass transfer between methane gas and background dissolved gases (e.g., nitrogen) to improve stray gas detection techniques and advance understanding of methane persistence following a repaired leak. This was achieved by conducting a series of gas injection experiments in a quasi-two-dimensional flow cell (40 × 39.6 × 1.15 cm) simulating an active gas leak and a post-repair scenario and developing simple single cell numerical models of the active (steady-state) leak and the post-repair (kinetic) dissolution. Experiments were conducted at two aqueous fluxes (3.8 m/day and 0.9 m/day) and two heterogeneities (pool- and finger-dominated source architectures). Dissolved oxygen was measured in the effluent water as a representative of background dissolved gases and light transmission techniques were used to quantify gas saturations. A steady-state model was developed to predict the mass transfer rate coefficient for each experiment and the changes in background dissolved gases under a range of conditions. A kinetic model was developed to predict the gas saturations and dissolved gas concentrations during post-repair dissolution, testing the sensitivity of mass transfer rate coefficients and single- and multi-component dissolved gases. Experiments showed that background dissolved gas detectability was highest at slow groundwater fluxes and in pooled source architectures. The steady-state model indicated that the detectability of background dissolved gases was proportional to the initial background dissolved gas concentration in the groundwater, however, the dissolved source gas concentrations remained relatively unchanged with depleted background dissolved gases. Experiments also showed that more time was required for background dissolved gases to return to baseline conditions post repair in pooled source architectures. Kinetic model simulations indicated that a constant mass transfer rate coefficient was sufficient to predict experimental data, as a transient mass transfer rate coefficient did not substantially improve the model fit. The kinetic model also demonstrated that gas persistence was longer in simulations that considered multiple dissolved gases compared to a single-component model. The findings of this study indicate that background dissolved gases may be a useful tool for stray gas detection and that gas persistence is influenced by multiple dissolved gases.
Co-Authorship

This thesis has been prepared in manuscript format. Chapter 2 “Laboratory investigation on the impacts of source architecture and aqueous velocity on background dissolved gas detectability during stray gas migration” was co-authored by M.M. Calvert and K.G. Mumford in preparation for submission to *Advances in Water Resources*. Scope and methods were developed by both authors. Experimental set up was developed by M.M. Calvert and K.G. Mumford, with input from A. Nunez Garcia. Data collection, modelling, analysis, and interpretation was conducted by M.M. Calvert with guidance from K.G. Mumford. The manuscript was written by M.M. Calvert and edited by K.G. Mumford.

Chapter 3 “Gas-water mass transfer: Investigating the impacts of mass transfer rate coefficients and multi-component dissolved gases on gas dissolution” was co-authored by M.M. Calvert and K.G. Mumford in preparation for submission to a peer-reviewed journal. Scope and methodologies were developed by both authors. Modeling, analysis, and interpretation were conducted by M.M. Calvert with guidance from K.G. Mumford. The manuscript was written by M.M. Calvert and edited by K.G. Mumford.
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<td>APS</td>
<td>Announced Pledges Scenario</td>
</tr>
<tr>
<td>CAPP</td>
<td>Canadian Association of Petroleum Producers</td>
</tr>
<tr>
<td>CCA</td>
<td>Council of Canadian Academies</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved Oxygen</td>
</tr>
<tr>
<td>GTP</td>
<td>Ganglia-to-Pool</td>
</tr>
<tr>
<td>IFA</td>
<td>Interfacial Area</td>
</tr>
<tr>
<td>LEA</td>
<td>Local Equilibrium Assumption</td>
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<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
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<tr>
<td>LNG</td>
<td>Liquified Natural Gas</td>
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<tr>
<td>LTM</td>
<td>Light Transmission Method</td>
</tr>
<tr>
<td>NAPL</td>
<td>Non-Aqueous Phase Liquid</td>
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<tr>
<td>NZE</td>
<td>Net Zero Emissions</td>
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<tr>
<td>PV</td>
<td>Pore Volume</td>
</tr>
<tr>
<td>SCVF</td>
<td>Surface Casing Vent Flow</td>
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<td>STEPS</td>
<td>Stated Policy Scenario</td>
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<tr>
<td>TDGP</td>
<td>Total Dissolved Gas Pressure</td>
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<tr>
<td>$A_{gw}$</td>
<td>Interfacial area between gas and water ($L^2$)</td>
</tr>
<tr>
<td>$A_{na}$</td>
<td>Interfacial area between non-aqueous and aqueous phase ($L^2$)</td>
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<tr>
<td>$b'$</td>
<td>Empirical fit parameter ($L^{-1}$)</td>
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<td>$b, c, d$</td>
<td>Empirical fit parameter (-)</td>
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<td>$c_g$</td>
<td>Gas concentration ($ML^{-3}$)</td>
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<td>$c_g^*$</td>
<td>Gas concentration at the interface between aqueous and non-aqueous phases ($ML^{-3}$)</td>
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<td>Aqueous concentration ($ML^{-3}$)</td>
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<td>Influent aqueous concentration ($ML^{-3}$)</td>
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<td>$c_w^*$</td>
<td>Aqueous concentration at interface between aqueous and non-aqueous phases ($ML^{-3}$)</td>
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<td>$D_m$</td>
<td>Molecular diffusion constant ($L^2T^{-1}$)</td>
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<td>$d_{50}$</td>
<td>Median particle diameter (L)</td>
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<tr>
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<td>Symbol</td>
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<td>$K^{Sh}$</td>
<td>Mass transfer rate coefficient calculated using the Sherwood correlation (T$^{-1}$)</td>
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<td>$K^{Sh}_L$</td>
<td>Lumped mass transfer rate coefficient calculated using the Sherwood correlation (L$^3$T$^{-1}$)</td>
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Chapter 1

Introduction

1.1 Background

1.1.1 Natural Gas Resources

Natural gas has been critical to the energy transition as it emits fewer greenhouse gas emissions than coal-generated electricity, and can be used across industrial, residential, and commercial applications (CAPP, 2022; CCA, 2014; Rivard et al., 2014). In 2020, natural gas supported approximately 37% of Canada’s energy demand, with Canada being the sixth largest producer globally (CAPP, 2022). Demand for natural gas has grown over the past decade, however, the future of natural gas is highly dependent on the implementation of net-zero emissions policies (IEA, 2021). If production continues at the current Stated Policy Scenario (STEPS), natural gas demand is expected to increase 15% by 2030 and 30% by 2050 (Figure 1.1a,c) (IEA, 2021). In the most drastic case (Net Zero Emissions by 2050 [NZE]), global demand is predicted to peak around 2025 and decline quickly by 2050 (Figure 1.1a,c) (IEA, 2021). Although demand is expected to decline, natural gas will still be necessary to displace coal power in emerging markets and developing economies and support low-carbon hydrogen production (Figure 1.1b) (IEA, 2021). This shift in demand by region generates export opportunities for North America (CAPP, 2022; IEA, 2021). Liquified natural gas (LNG) is natural gas cooled to -161°C, reducing its volume for safer and efficient transport by ship (CAPP, 2022). LNG export growth is predicted to increase by 46% from 2021 to 2025 in North America, accounting for more than half of the LNG export growth globally (IEA, 2022).
Natural gas is composed primarily of methane, with smaller quantities of hydrocarbons such as ethane, butane, and propane, as well as other non-hydrocarbon gases such as carbon dioxide and oxygen (CAPP, 2022; CCA, 2014; Molofsky et al., 2021). It is found in deep, organic-rich sedimentary formations either in porous formations overlain by a tight impermeable cap rock (conventional natural gas) or trapped within tight shale formations (unconventional natural gas) (CCA, 2014; Howarth, 2019). Technological advancements such as horizontal drilling and hydraulic fracturing, have made tight shale formations economical to produce (CCA, 2014; Howarth, 2019; Rivard et al., 2014). Natural gas formations exist in most Canadian provinces, with current production occurring primarily in the Western Sedimentary Basin in Saskatchewan, Alberta, and British Columbia (Figure 1.2) (CAPP, 2022; CCA, 2014; Rivard et al., 2014).
1.1.2 Well Construction and Stray Gas Sources

Natural gas production zones range from two to three kilometers in depth and can reach hundreds of meters in the lateral direction from the vertical wellbore (CAPP, 2022; CCA, 2014). A production well typically passes through a shallow zone containing fresh groundwater used for drinking or agricultural purposes, an intermediate zone that may contain a mixture of saline water and oil and gas uneconomical for production, and a deep zone containing the target formation (Dusseault & Jackson, 2014). Production wells consist of nested layers of steel casing and cement to create a barrier between the well and the shallower water resources (Figure 1.3) (Bachu, 2017; CAPP, 2022; CCA, 2014; Lackey et al., 2017). It is crucial that the cement and casing are properly set to prevent cross-contamination between hydrocarbons and drilling fluids.
from deep or intermediate zones and water in the shallow zone or atmosphere (CCA, 2014; Lackey et al., 2017).

Figure 1.3: Schematic of a well head and nested casing and cement layers through various zones in the subsurface (Modified from Bachu (2017)).

Gases that migrate up the well anulus are either released to the atmosphere as surface casing vent flow (SCVF) or trapped in the annulus if the well head valve is shut (Lackey et al., 2017). The unintentional release of gas into the subsurface, referred to as stray gas, is often a result of deterioration at the cement-casing or cement-rock wall interface which creates pathways through which gas can flow (Bachu, 2017; Dusseault & Jackson, 2014; Molofsky et al., 2021). Flaws in cement can occur due to poor construction, changes to downhole conditions, or deterioration over time leading to possible gas migration in producing, decommissioned, and abandoned wells (Bachu, 2017; Dusseault & Jackson, 2014; Gorody, 2012). Abandoned wells in particular have proven to contribute considerably to stray gas migration (Bachu, 2017).
and methane emissions (Kang et al., 2014) likely because construction occurred prior to current regulatory standards, and involved older drilling materials and technology (Bachu, 2017).

Over the last decade, public concerns regarding environmental impacts of natural gas production have grown, specifically regarding greenhouse gas emissions and surface water and groundwater contamination (CCA, 2014; Dusseault & Jackson, 2014; Vengosh et al., 2014). Although dissolved methane itself is not harmful to human health (Molofsky et al., 2021), elevated levels in groundwater can cause changes to water chemistry by mobilizing dissolved metals and altering redox conditions (Cahill et al., 2017; Schout et al., 2018; Schwartz, 2015; Van Stempvoort et al., 2005; Vengosh et al., 2014). When exsolved from groundwater, methane can pose explosion or asphyxiation risks and can contribute to greenhouse gas emissions when released to the atmosphere (Abboud et al., 2021; El Hachem & Kang, 2022; Molofsky et al., 2021; Vengosh et al., 2014; Williams et al., 2021). Methane gas is 80.8 to 82.5 times stronger than carbon dioxide in a 20-year time period, contributing significantly to heat trapping and global warming (El Hachem & Kang, 2022).

1.1.3 Stray Gas Migration Dynamics

Gas migration patterns depend on gas flow rate and porous media grain size. Gas migration can exhibit connected or continuous channels (fine grained, high flow rates), discontinuous channels (coarse grained, low flow rates) or a combination of both characteristics, referred to as transitional flow (Geistlinger et al., 2006; Ji et al., 1993; Van De Ven & Mumford, 2019). As gas injection rates increase, migration tends to shift from a single finger-like channel to U- or V-shaped migration patterns comprised of multiple connected gas channels (Geistlinger et al., 2006; Ji et al., 1993; Van De Ven & Mumford, 2019). The nature of these gas channels is a function of the competition between viscous, capillary, and buoyancy forces (Brooks et al., 1999; Elder & Benson, 1999; Geistlinger et al., 2006; Glass et al., 2001; Ji et al., 1993). Due to a lower viscosity and density than water, methane gas migrates quickly and primarily vertically through the porous media (Molofsky et al., 2021). As gas migrates, the capillarity of the porous media causes lateral deviations
in migration pathways, resulting in tortuous rather than straight pathways, as gas preferentially occupies larger pore spaces first (lower capillary pressures) (Ji et al., 1993; Molofsky et al., 2021; Van De Ven & Mumford, 2020a).

Gas migration is further complicated by subsurface heterogeneities. Capillary barriers (e.g., finer grained lenses) require higher entry pressures for gas to invade the pore space, causing gas to pool beneath the barriers until pool heights are great enough to exceed entry pressures (Figure 1.4) (Glass et al., 2001; Ji et al., 1993). Due to its low viscosity, gas can easily migrate laterally beneath capillary barriers until it reaches the edge of the lens where it then spills over and continues migrating upwards (Van De Ven & Mumford, 2020c). Therefore, subsurface heterogeneities, even small-scale variations in permeability, can influence gas migration pathways considerably (Cahill et al., 2018; Van De Ven et al., 2020). Conversely, structural features (e.g., faults or fracture networks) can create high permeability pathways that allow for preferential flow of stray gas from one area to another (Kissinger et al., 2013; Nowamooz et al., 2015; Vengosh et al., 2014). Field studies (Cahill et al., 2018), laboratory experiments (Davidson et al., 2022; Glass et al., 2001; Van De Ven & Mumford, 2020b), and numerical models (Kissinger et al., 2013; Moortgat et al., 2018; Nowamooz et al., 2015) have all been used to study gas migration in the presence of heterogeneity or high permeability conduits.

There are two primary expressions of methane in the stray gas migration conceptual model. Gas that reaches the surface and is emitted to the atmosphere is referred to as a surface expression. Free-phase gas that is trapped in the subsurface and interacts with groundwater to generate dissolved gas plumes is referred to as an aqueous expression. Gas migration through the subsurface is a complex combination of free-phase gas, in the form of pools and finger-like formations, and dissolved gas plumes (Figure 1.4) (Molofsky et al., 2021; Van De Ven & Mumford, 2020a).
Figure 1.4: Conceptual model of stray gas migration in fractured bedrock and unconsolidated sand aquifers (Molofsky et al., 2021).

1.1.4 Monitoring and Detection

Current monitoring methods are highly dependent on surface expressions. Gas migration is primarily identified by the presence of bubbling in surface water surrounding wellheads, distressed or dead vegetation, odors or combustible gas not attributed to other sources, and high SCVF rates (>300 m$^3$/day) (Alberta Energy Regulator, 2021; Bachu, 2017; BC Oil and Gas Commission, 2021). If a leaky well is suspected, additional investigations may be conducted. This may include H$_2$S detection, ground surface methane detection, shallow gas surveys, and groundwater sampling for elevated dissolved methane concentrations, however, sampling methods, location, and duration, as well as action level thresholds vary by province and state and chemical signals measured in the groundwater are often susceptible to degradation (e.g., oxidation of dissolved methane) (BC Oil and Gas Commission, 2021; Molofsky et al., 2021).
Phased monitoring approaches are recommended, taking advantage of both surface and aqueous expressions and a variety of analytical tools (McIntosh et al., 2019; Ryan et al., 2015). Investigations may include a combination of isotopic analyses of dissolved gas compositions, hydrocarbon ratios, static gas chamber measurements, and high resolution gas profiles (McIntosh et al., 2019; Osborn et al., 2011; Schout et al., 2019; Van Stempvoort et al., 2005). Emerging research also suggests background dissolved gases such as nitrogen or carbon dioxide may be useful as a potential indicator of stray gas migration due to the multi-component exchange of free-phase gas and dissolved gases generating elevated background dissolved gas concentrations and depleted dissolved methane concentrations in the groundwater downstream of a leaking well (Forde et al., 2019), however, there have been no field, laboratory, or modelling studies that have focused on the role of background dissolved gases for the investigation of stray gas migration. Nitrogen in particular may be a useful indicator because of its abundance and low reactivity compared to methane.

It is necessary for multiple tools to be utilized during monitoring as methane signatures in both the gas and aqueous phases can become altered due to biodegradation, reducing or oxidizing conditions, or mixing with other gases (Gorody, 2012; McIntosh et al., 2019; Schout et al., 2019). They can also be missed entirely due to spatially and temporally inconsistent surface expressions (Cahill et al., 2017; Forde et al., 2019; Van De Ven & Mumford, 2020c). Subsurface heterogeneities can cause leaking gas to surface at considerable distances (>10 m) from the leaking well due to lateral migration along capillary barriers or preferential flow through high permeability faults or fractures, and in some cases, migration to surface can be prevented completely due to heterogeneities or dissolution (Cahill et al., 2018; Forde et al., 2019; Schout et al., 2020).

1.1.5 Mass Transfer

Interactions between the groundwater and the free-phase gas create dissolved methane plumes which can be transported great distances from the leak source, and are explained through the fundamentals of gas-water mass transfer (Cahill et al., 2018; Schout et al., 2020). Dissolution of methane depends primarily on
gas solubility (25 mg/L at 20°C and 1 atm), gas-water interfacial area (IFA), multi-component mass transfer, and groundwater velocity relative to the gas flow rate (Molofsky et al., 2021).

The rate of mass transfer can be described as a function of a driving force and an IFA:

\[
J = \frac{1}{A_{na}} \frac{dm}{dt} = k_w (c_w^* - c_w)
\]  

(1.1)

where \( J \) is a mass flux of gas to aqueous phase, \( A_{na} \) is the IFA between the aqueous and non-aqueous (i.e., gas) phase, \( \frac{dm}{dt} \) is the mass rate of change for the aqueous phase, \( k_w \) is the mass transfer coefficient (L/T), \( c_w^* \) is the aqueous phase concentration at solubility, and \( c_w \) is the aqueous phase concentration in the bulk solution (Miller et al., 1990). IFA is difficult to quantify as it changes with time as the gas dissolves, and source architecture can cause certain areas of the gas phase to be more accessible to flowing water than others (Miller et al., 1990). Therefore, mass transfer models commonly use a lumped mass transfer rate coefficient, which groups the IFA and the mass transfer coefficient, to avoid directly quantifying the IFA (Kokkinaki et al., 2013; Miller et al., 1990; Saba & Illangasekare, 2000; Zhu & Sykes, 2000). Sherwood correlations are commonly used in the non-aqueous phase liquid (NAPL) literature to determine the lumped mass transfer rate coefficient expressed as a function of fluid saturation, Reynolds number, and empirically fit coefficients (Imhoff et al., 1994; Kokkinaki et al., 2013; Miller et al., 1990; Nambi & Powers, 2003; Powers et al., 1994; Saba & Illangasekare, 2000).

At slow aqueous fluxes, proposed to be < 4 m/day for trapped gases (Geislinger et al., 2005), mass transfer is traditionally simplified with the local equilibrium assumption (LEA) which assumes that mass transfer is instantaneous between the aqueous and non-aqueous phase such that the two phases are in thermodynamic equilibrium and mass transfer kinetics can be neglected (Fry et al., 1996; Geistlinger et al., 2005). Alternatively, at fast aqueous fluxes, mass transfer is rate-limited, meaning it depends on the concentration gradient between the bulk aqueous phase and the non-aqueous phase interface and kinetics cannot be ignored (Geller & Hunt, 1993; Miller et al., 1990).
Gas-water mass transfer studies have evolved over time, including the use of single-component constant volume models looking at the retardation of dissolved gases due to trapped gas (Donaldson et al., 1997; Fry et al., 1995, 1996), multi-component LEA models (Amos & Mayer, 2006; Cirpka & Kitanidis, 2001; Mumford et al., 2010), and multi-component variable gas volume models (Geistlinger et al., 2006; Holocher et al., 2003). Cirpka and Kitanidis (2001) demonstrated the importance of considering multiple dissolved components, describing a competition between all components for space in the gas phase. This competition is dictated by the partial pressure of each phase, causing gas saturations and dissolved concentrations to change accordingly (Cirpka & Kitanidis, 2001; Van De Ven & Mumford, 2020b). Therefore, concentrations of one component of interest cannot be interpreted or simulated accurately without the consideration of the others (Cirpka & Kitanidis, 2001). Mass transfer has been directly applied to stray gas modelling to demonstrate methane gas and dissolved methane plume migration behaviour over time (Roy et al., 2016; Schout et al., 2020), however, these models are often simplified by considering only a single gas component.

1.2 Research Needs and Objectives

Stray gas migration has shown to be prevalent in producing and decommissioned wells, which suggests an ongoing threat to groundwater resources, regardless of production status. To better understand the environmental impacts of methane contamination to groundwater, interactions between the free-phase gas and the groundwater must be better understood. There is a need to investigate the role of background dissolved gases in a stray gas context to properly detect, monitor, and regulate stray gas migration. This can also provide insight into the persistence of methane gas and the post-repair recovery of aquifers contaminated by stray gas.

The goal of this research was to investigate the effects of multi-component mass transfer between methane gas and background dissolved gases to improve stray gas detection techniques and further understand methane persistence in a post-repair state. This was achieved through a series of intermediate-scale
laboratory experiments and numerical models of active (steady state) leaks and post-repair (kinetic) dissolution. The specific objectives were to:

1. Investigate the changes in background dissolved gases during an active leak and post-repair scenario, specifically exploring the impact of source architecture (heterogeneity) and groundwater flow rate on the background dissolved gas detectability. This objective was addressed through a series of intermediate-scale laboratory experiments monitoring dissolved oxygen during an active gas leak and post-repair scenario, in two different heterogeneous sand packs (branched and pool dominated) and at two different flow rates (fast and slow). A steady-state model was also developed to predict changes in detectability at conditions different than those used in the experiments (e.g., depleted influent conditions) (Chapter 2).

2. Investigate the role of mass transfer kinetics in stray gas dissolution modelling. This objective was addressed by fitting a Sherwood correlation to the experimental data and comparing it to Sherwood correlations developed for NAPL-water systems (Chapter 3) and using a kinetic dissolution model developed to predict post-repair dissolution in simulations using constant and transient mass transfer rate coefficients (Chapter 3).

3. Investigate the impact of multiple dissolved gas components on the dissolution of trapped gas. This objective was addressed using the kinetic model, running simulations with a single- and a multi-component system (multiple dissolved gases) and comparing predicted gas saturations and dissolved gas concentrations over time (Chapter 3).

This research aims to improve understanding of multi-component partitioning in a stray gas context to improve monitoring and detection tools and modeling of methane persistence, ultimately leading to improved detection and understanding of stray gas impacts on groundwater environments.
1.3 Thesis Organization

The following thesis has been prepared in manuscript format. The subsequent chapters (Chapter 2 and 3) have been prepared with the intent of submission to peer-reviewed academic journals. Each chapter includes an Introduction such that results and objectives are supported by previous literature. Chapter 2 presents laboratory experiments and a steady-state model for analyzing the active gas injection stage. Chapter 3 presents the Sherwood correlation and kinetic dissolution model developed for the purpose of investigating methane persistence. Chapter 4 summarizes the overall conclusions and recommendations for applications of the work and further research. The appendix includes additional experimental results and model simulations. Due to the nature of the manuscript format some material from the introduction in Chapter 1 may overlap with the introductions in Chapter 2 and 3.

1.4 References


CCA. (2014). Environmental impacts of shale gas extraction in Canada.


Chapter 2

Laboratory investigation on the impacts of source architecture and aqueous velocity on background dissolved gas detectability during stray gas migration

2.1 Background

As conventional and unconventional production methods increase to meet global energy demands, stray gas migration from leaky natural gas wells and the associated environmental impacts on drinking water sources and contributions to greenhouse gas emissions have been a recent point of discussion (CCA, 2014; Lackey et al., 2017; Schout et al., 2020). Compromised well casing or deteriorating cement can create preferential pathways for gas to migrate from production formations directly to surface through surface casing vent flow (SCVF) or into shallow aquifers as stray gas (Dusseault & Jackson, 2014; Jackson et al., 2013; Kang et al., 2014; Lackey et al., 2017; Vengosh et al., 2014). Stray gas can originate from producing, decommissioned, and abandoned wells, therefore the potential for contamination may continue after production ceases (Bachu, 2017; Dusseault & Jackson, 2014; Gorody, 2012; Jackson et al., 2013; Kang et al., 2014). Gas migration studies, related to stray gas as well as other gas injection applications such as air sparging, performed both in the laboratory (Geistlinger et al., 2006; Glass et al., 2001; Ji et al., 1993; Stöhr & Khalili, 2006; Van De Ven et al., 2020) and field (Cahill et al., 2018; Forde et al., 2019), describe stray gas pathways as continuous channels and discontinuous ganglia. Gas moves upward due to buoyancy forces and is highly sensitive to heterogeneities, which cause gas pooling and lateral migration beneath capillary barriers (Cahill et al., 2018; Forde et al., 2018). Studies have also shown that mass transfer from free-phase gas creates dissolved gas plumes (Figure 2.1) (Cahill et al., 2018; Schout et al., 2020; Van De Ven & Mumford, 2020c).

The primary component of natural gas is methane (Gorody, 2012; Jackson et al., 2013), which is not known to be harmful to human health (Molofsky et al., 2021). However, elevated methane levels in groundwater can change water chemistry by mobilizing dissolved metals and altering redox conditions (Cahill et al., 2018).
When exsolved from groundwater, methane can pose explosion and asphyxiation risks (Abboud et al., 2021; Jackson et al., 2013; Molofsky et al., 2021; Osborn et al., 2011; Vengosh et al., 2014) and when released to the atmosphere contributes to greenhouse gas emissions (Abboud et al., 2021; El Hachem & Kang, 2022; Kang et al., 2014; Molofsky et al., 2021; Vengosh et al., 2014; Williams et al., 2021).

Current leaky well detection methods rely heavily on surface expressions such as high SCVF rates, bubbling in nearby surface water, and distressed or dead vegetation (Alberta Energy Regulator, 2021b; Bachu, 2017; CCA, 2014). If stray gas migration is suspected, additional phased analytical approaches can be performed around the suspected well (McIntosh et al., 2019). Analyses may include the use of surface efflux chambers, aqueous sampling for dissolved methane, and isotopic analysis. However, these tools can often be unreliable due to spatially and temporally inconsistent surface expressions and chemical or biological alterations to aqueous expressions (Forde et al., 2018; Jackson et al., 2013; Van De Ven & Mumford, 2020c). Uncertainties in surface expressions make it difficult to know when and where to look for initial signs of gas migration. For example, low permeability lenses can cause extensive lateral gas migration and gas breakthrough at surface far from wellheads, and can prevent gas from reaching the surface in some cases (Cahill et al., 2017, 2018; Forde et al., 2019). The reliance on surface expressions for stray gas detection is concerning as surface expressions are not always indicative of the subsurface conditions (Cahill et al., 2017; Van De Ven & Mumford, 2020a). Additionally, degradation pathways such as methane oxidation can alter the composition of aqueous expressions such that sampling does not indicate the full extent of subsurface gas migration (Forde et al., 2019; Molofsky et al., 2021; Schout et al., 2018; Van Stempvoort et al., 2005). There is a need for a complementary monitoring tool that considers a naturally abundant chemical signal less susceptible to degradation to improve the detectability of stray gas leaks (Ryan et al., 2015).

Studies have shown that multi-component mass transfer between stray gas and dissolved gases can influence the surface and aqueous expressions (Van De Ven & Mumford, 2020a, 2020b, 2020c). Free-phase methane
and dissolved background gases in the groundwater, such as nitrogen or oxygen, exchange to satisfy Henry’s Law and Dalton’s Law (Cirpka & Kitanidis, 2001; Geistlinger et al., 2005; Van De Ven & Mumford, 2020a). Although this exchange has been acknowledged in the literature, few have investigated the suitability of using background gases as a monitoring tool for stray gas migration (Forde et al., 2019; Larson et al., 2018).

One field study by Forde et al. (2019) sampled groundwater for dissolved methane, carbon dioxide, and nitrogen during and after a controlled methane release at the Canadian Forces Base Borden site. The study showed that during an active methane leak, concentrations of dissolved methane increased, and dissolved nitrogen decreased. When gas injection was stopped, dissolved methane concentrations decreased and dissolved nitrogen concentrations rebounded to and exceeded baseline conditions (Forde et al., 2019). This work showed that changes in background dissolved gases due to multi-component mass transfer with the free-phase gas are measurable at the field scale and may be a useful tool to include in the phased analytical monitoring approach to detect leaking wells. It is also suggested that this response may be useful as an indicator of complete dissolution of free-phase methane (Forde et al., 2019).

Before background dissolved gases can be integrated into a monitoring approach, their response and detectability during an active leak and post-repair must be better understood. The objective of this study was to investigate the conditions that influence background dissolved gas detectability, specifically looking at the impact of source architecture and groundwater flow rate on the background dissolved gas response. A series of laboratory scale experiments were conducted, monitoring background dissolved gases in two different heterogeneous sand packs at different groundwater flow rates during and after an active gas leak. The light transmission method (LTM) was used to quantify local gas saturations throughout the experiment. A steady-state numerical model was also developed to predict changes in background dissolved gases under a range of input conditions during an active gas leak.
Figure 2.1: Conceptual model of stray gas migration from a leaking natural gas well in a shallow aquifer modified from Molofsky et al. (2021).

2.2 Methods and Materials

2.2.1 Flow Cell

All experiments were conducted in a quasi-two-dimensional flow cell consisting of two 5 mm thick glass panes held together by an aluminium frame and neoprene O-rings. Internal dimensions of the cell measured 40 × 39.6 × 1.15 cm (Figure 2.2). Clear wells were created at both the influent and effluent edges of the cell by inserting a U-channel equal to the height of the cell wrapped in an 80-mesh screen, and promoted uniform boundary conditions. Water was pumped into the cell through five ports on the influent side and exited through one port on the effluent side. Five ports along the bottom of the cell were fitted with water-
wet 80 µm hydrophilic nylon filters (Nylon Net Filter, NY8004700) to allow drainage under vacuum. A 26-gauge stainless-steel needle was inserted in the sixth port (middle right) for gas injection.

Figure 2.2: Experimental set up showing the flow cell, gas injection apparatus, and aqueous sampling flow-through cell

2.2.2 Sand Packing

Heterogeneous sand packs for all experiments were created using a modified 3D printer technique described in Davidson et al. (2022). The 3D printer acted as an automated hopper system that deposited sand mixtures into the flow cell in herringbone cross bed formations, following the general approach established by Krishnamurthy et al. (2019). Combinations of 20-30 and 30-40 or 20-30 and 40-60 (4:1 by mass) mesh size silica Accusand (Schroth et al., 1996), which have been used for previous LTM studies (Davidson et al., 2022; Glass et al., 2001; Niemet & Selker, 2001; Van De Ven et al., 2020), were mixed to create packs with two different degrees of heterogeneity (Figure 2.3). For the remainder of the discussion, these packs will be referred to by the finest grade sand in each mixture, therefore the 20-30/30-40 mixture and the 20-30/40-60 mixture will be referred to as 3040 and 4060, respectively.
Sand mixtures were washed with deionized water to remove any fine particulates and dried prior to packing. Dry sand was placed into the hopper and turned end over end to mix (Davidson et al., 2022). Three stacked layers of cross beds, each approximately 10 cm high, were deposited followed by a 7 cm normally graded layer on top. The glass was tapped with a rubber mallet to compact the dry sand. Each of the dry packs was flushed with CO\textsubscript{2} gas through the bottom ports for 2 hours at a flow rate of 1000 mL/min (Krishnamurthy et al., 2019) and then immediately flushed with 4 pore volumes of vacuum degassed deionized water to dissolve any trapped CO\textsubscript{2} gas bubbles. The cell was tapped again with the rubber mallet to compact grains further. A mesh geomembrane, followed by a 2 cm layer of 5 mm stainless-steel ball bearings were placed on the top of the sand to minimize grain rearrangement of the top layer during gas breakthrough (Figure 2.2).

![Image of cross bedded sand packs](image)

**Figure 2.3:** Saturated a) 3040 and b) 4060 cross bedded sand packs backlit by an LED light panel.

### 2.2.3 Aqueous Flow and Gas Injection

Experiments were conducted at two aqueous fluxes, 3.8 m/day and 0.9 m/day, referred to as fast (F) and slow (S), respectively (Table 2.1) using a peristaltic pump (Masterflex L/S 1-100 RPM cartridge pump). Aqueous fluxes were selected to be less than reported velocity thresholds for local equilibrium assumptions (<4 m/day) in 1D gas injection experiments (Geistlinger et al., 2006). Mass transfer is also not sensitive to velocity changes at slow flow rates (below approximately 0.1 m/day) as discussed in section 2.3.3. Each
experiment consisted of three stages: 1) baseline, 2) active gas leak, and 3) post-repair. In Stage 1, 2 pore volumes of deionized water equilibrated with the atmosphere was pumped through the cell to displace any dissolved CO$_2$ remaining from the saturation procedure and to establish a baseline condition. Prior to injecting gas, the water table was raised above the ball bearings by closing the outlet valve so that bubbling at initial gas breakthrough could be seen. The pump was then stopped and gas was injected until breakthrough using changes in the water table height to calculate the total gas volume emplaced. This initial gas injection was used to calibrate the LTM.

**Table 2.1: Summary of experiments.**

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Darcy Flux (m/day)</th>
<th>Coarse Sand</th>
<th>Fine Sand</th>
<th>Porosity (-)</th>
<th>GTP Ratio</th>
<th>Active Leak</th>
<th>Post-Repair</th>
</tr>
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<tbody>
<tr>
<td>3040F-1</td>
<td>4.2</td>
<td>20-30</td>
<td>30-40</td>
<td>0.33</td>
<td></td>
<td>1.44</td>
<td>10.55</td>
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<tr>
<td>3040F-2</td>
<td>3.9</td>
<td>20-30</td>
<td>30-40</td>
<td>0.33</td>
<td></td>
<td>1.08</td>
<td>9.92</td>
</tr>
<tr>
<td>3040F-3</td>
<td>3.9</td>
<td>20-30</td>
<td>30-40</td>
<td>0.33</td>
<td></td>
<td>0.73</td>
<td>2.47</td>
</tr>
<tr>
<td>3040S-1</td>
<td>0.9</td>
<td>20-30</td>
<td>30-40</td>
<td>0.33</td>
<td></td>
<td>2.70</td>
<td>11.40</td>
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<tr>
<td>3040S-2</td>
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<td>20-30</td>
<td>30-40</td>
<td>0.33</td>
<td></td>
<td>2.87</td>
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<tr>
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<td>30-40</td>
<td>0.33</td>
<td></td>
<td>2.16</td>
<td>5.31</td>
</tr>
<tr>
<td>4060F-1</td>
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<td>40-60</td>
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<td></td>
<td>0.67</td>
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<td></td>
<td>0.29</td>
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</tr>
<tr>
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<td>40-60</td>
<td>0.31</td>
<td></td>
<td>0.21</td>
<td>1.33</td>
</tr>
<tr>
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<tr>
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<td>40-60</td>
<td>0.32</td>
<td></td>
<td>0.19</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Argon gas was used as a surrogate for methane in this study. Argon and methane have the same Henry’s constant, therefore, the mass transfer behaviours are assumed to be the same (Sander, 2015). Argon gas was injected in the bottom of the cell at 10 mL/min using a mass flow controller (Cole Parmer, RK-32907-55). A gas flow rate of 10 mL/min corresponds to the lower end of reported SCVF rates (Alberta Energy Regulator, 2021a; Nowamooz et al., 2015). At the beginning of Stage 2, the outlet was opened to allow the water table to drop to approximately 1 cm below the top of the sand before aqueous flow was re-established. The water table was set below the top of the sand to ensure flow did not bypass the sand by moving through
the higher permeability layer of ball bearings. Gas injection continued throughout Stage 2 to simulate an active gas leak until 5 pore volumes of deionized water were pumped through the cell.

The gas injection was stopped at the beginning of Stage 3, representing a successful well repair. Deionized water was continuously pumped through the cell for 7 pore volumes and 13 pore volumes for the 3040 and 4060 experiments, respectively.

2.2.4 Effluent Sampling and Measurements of Gas Saturation

The effluent water flowed into a flow-through cell where a polarographic dissolved oxygen (DO) probe (Hanna Instruments, HI764080) was secured through a rubber stopper (Figure 2.2). DO concentrations in the effluent water were measured at intervals of 2 or 5 min, depending on the test duration. The flow-through cell was sealed and had no headspace. Due to variations in DO solubility with temperature, measured DO concentrations were normalized to the ratio of the solubility of oxygen at the average temperature of the experiment to the average measured DO concentration of the influent water, to allow for comparison between experiments. DO was measured in these experiments as representative of background dissolved gases given that no degradation was taking place, and because it can be easily measured in the controlled laboratory setting. It is expected, however, that other gases (e.g., nitrogen, argon) would be more suitable to measure in field applications due to their lower reactivity than oxygen in field settings. Nitrogen is included in the model discussed in section 2.2.5.

Gas saturations were measured using an LTM technique, which is based on transmitted light intensity as (Niemet & Selker, 2001):

$$S_g = 1 - \left( \frac{\ln(I/I_s)}{\ln(I_r/I_s)} (1 - S_r) + S_r \right)$$

(2.1)

where $S_g$ is the gas saturation, $I$ is the light intensity measured through the sand, $I_s$ the light intensity transmitted through water-saturated sand, $I_r$ is the light intensity transmitted through sand at residual wetting
saturation, and $S_r$ is the residual saturation. A calibrated $I_r/I_s$ value rather than a measured $I_r/I_s$ was used to avoid underestimations of gas volumes in gravity destabilized gas flow (Van De Ven et al., 2020) and was fit to displaced water volumes measured during the initial gas injection. Calibrated $I_r/I_s$ values were $0.33 \pm 0.06$, consistent with fitted values used in previous studies in similar sand packs by Davidson et al. (2022). The gas saturation detection limit was 0.02 as determined by analyzing variations in transmitted light intensity in known gas-free regions (Van De Ven & Mumford, 2019).

Images of the cell were captured using a Canon Rebel T6i (Canon EF-S 18-55mm lens) at a 0.1 mm × 0.1 mm resolution, and upscaled to a resolution of 1 mm × 1 mm before applying Eq 2.1 to reduce noise (Van De Ven et al., 2020). The cell was backlit with an LED panel (Ledgo LG-S150M StudioStream 150W Daylight Panel Light). The light, camera, and cell were covered in blackout fabric to minimize reflections on the cell face. Images were captured in 5 s intervals during the initial gas injection, and every 10-30 min for the remainder of the experiment.

The architecture of the injected gas was classified using the ganglia-to-pool (GTP) ratio (Christ et al., 2010; Kokkinaki et al., 2013), calculated as the total volume of gas in the ganglia divided by the total volume of gas in the pools. Ganglia were defined as $S_g \leq 0.14$ for the 3040 pack and $S_g \leq 0.20$ for the 4060 pack based on the residual gas saturations ($S_{gr}$) measured following a drainage and imbibition event (Davidson et al., 2022). Using the LTM, gas volumes were calculated for each discretized grid of the evaluated image. A sum of the gas volume for grids with saturations less than $S_{gr}$ was calculated, resulting in the total volume of gas found in the ganglia formations. The volume of gas in grids that had gas saturations above $S_{gr}$ were summed, resulting in the total volume of gas found in the pooled formations. Although different thresholds have been used to define pool or ganglia dominated source zones (Christ et al., 2010), for this study, pooled source zones refer to GTP < 1 and ganglia or branched source zones refer to GTP > 1. GTP ratios were calculated at the end of the active gas leak (end of Stage 2) just before gas injection was stopped, and at the end of the post-repair dissolution (end of Stage 3) (Table 2.1).
2.2.5 Steady-State Model

A simple steady-state model was developed to predict the aqueous and gas concentrations of three components (O₂, N₂ and Ar in the experiments) and estimate the response of background dissolved gases during an active gas leak for a range of possible site conditions. The model treats the flow cell as one grid block and tracks the aqueous and gas phases for each of the components of interest into and out of the cell.

The steady-state mass balance expressions for the aqueous and gas phases are:

\[ c_{w_j}Q_w = c_{w_j}Q_w - k_w A_{gw} \left( c_{w_j}^* - c_{w_j} \right) \]  \hspace{1cm} (2.2)

\[ m_{g_j} = c_{g_j}Q_g - k_g A_{gw} \left( c_{g_j}^* - c_{g_j} \right) \]  \hspace{1cm} (2.3)

where \( w \) refers to the aqueous phase and \( g \) refers to the gas phase, \( j \) refers to the component of interest, \( c_{w_j}^i \) is the influent concentration, \( Q_w \) is the aqueous flow rate, \( Q_g \) is the gas flow rate out of the cell, \( c_{w_j} \) is the concentration of component \( j \), \( k \) is the mass transfer coefficient (L/T), \( A_{gw} \) is the interfacial area between the gas and water phases, \( c_{w_j}^* \) is the concentration at the gas-water interface, and \( m_{g_j} \) is the mass flow rate of gas injected. The mass flow rate can be described using the ideal gas law:

\[ m_{g_j} = \frac{P_{inj}^i Q_{g_j}^i}{RT} \frac{c_{w_j}^*}{M_j} \]  \hspace{1cm} (2.4)

where \( P_{inj}^i \) is the gas injection pressure, \( Q_{g_j}^i \) is the volumetric gas injection rate into the cell, \( R \) is the ideal gas constant, \( T \) is the temperature, and \( M_j \) is the molar mass of component \( j \). Given that the mass of each component leaving one phase must enter the other:

\[ k_w A_{gw} \left( c_{w_j}^* - c_{w_j} \right) = k_g A_{gw} \left( c_{g_j}^* - c_{g_j} \right) \]  \hspace{1cm} (2.5)

allows Eq. 2.2 and 2.3 to be re-written as:
\[ c_{wj}^i Q_w = c_{wj} Q_w - K_L \left( c_{wj}^* - c_{wj} \right) \]  
(2.6)

\[ \dot{m}_{gj} = c_{gj} Q_g - K_L \left( c_{wj}^* - c_{wj} \right) \]  
(2.7)

where \( K_L \) is the lumped mass transfer rate coefficient (L^3/T), lumping together the mass transfer coefficient and the interfacial area. Further assuming that the gas phase is well mixed (i.e., \( c_{wj}^* \) is in equilibrium with \( c_{gj} \)), Eq. 2.6 and 2.7 are coupled using Henry’s Law:

\[ c_{wj}^* = c_{gj} H_j \]  
(2.8)

where \( H \) is the Henry’s coefficient, unique for each component of interest (Sander, 2015), and Dalton’s Law:

\[ P_T = RT \sum \frac{c_{gj}}{M_j} \]  
(2.9)

where \( P_T \) is the total gas pressure.

The model defined by Eq. 2.6-2.9 was used for two sets of calculations in this study. In each set, the system of 10 equations was solved for 10 unknowns. First, the model was used to estimate \( K_L \) for each experiment given known values of \( H, R, T, P_T, Q_w \) and \( \dot{m}_{gj} \) as well as a known influent water composition (measured \( c_{wO2}^i \) and \( c_{wN2}^i \) from a lookup table at the experimental temperature and pressure (Weiss, 1970)) and measured \( c_{wO2} \) at steady state. The solution of this system of equations also provides estimates of \( c_{gN2,O2,Ar}, c_{wN2,Ar} \) and \( Q_g \) (Table 2.2).
Table 2.2: Summary of steady-state model inputs and outputs for three sets of calculations.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Experiment Simulations</th>
<th>$K_L$ Simulations</th>
<th>Depleted Influent Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{wO_2}$ (mg/L)$^b$</td>
<td>8.53-9.02</td>
<td>8.74</td>
<td>0</td>
</tr>
<tr>
<td>$c_{wN_2}$ (mg/L)$^b$</td>
<td>14.00-14.62</td>
<td>14.41</td>
<td>17.9, 14.4, 10.8, 7.2</td>
</tr>
<tr>
<td>$c_{wAr}$ (mg/L)$^c$</td>
<td>3.32-6.01</td>
<td>Output</td>
<td>Output</td>
</tr>
<tr>
<td>$c_{wO_2}$ (mg/L)$^b$</td>
<td>Output</td>
<td>Output</td>
<td>Output</td>
</tr>
<tr>
<td>$c_{wN_2}$ (mg/L)</td>
<td>Output</td>
<td>Output</td>
<td>Output</td>
</tr>
<tr>
<td>$K_L \times 10^{-6}$ m$^3$/min</td>
<td>Output</td>
<td>6.2, 2.6, 0.11, 3.9</td>
<td>6.02</td>
</tr>
<tr>
<td>$Q_w$ (mL/min)</td>
<td>2.5, 10.4</td>
<td>0.001-275</td>
<td>0.001-275</td>
</tr>
<tr>
<td>$\dot{m}_g \times 10^{-6}$ mg/min</td>
<td>4.34</td>
<td>4.34</td>
<td>4.34</td>
</tr>
<tr>
<td>$P_T$ (Pa)</td>
<td>100000</td>
<td>100000</td>
<td>100000</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>298</td>
<td>298</td>
<td>298</td>
</tr>
<tr>
<td>$H_{O_2}$(-)$^d$</td>
<td>0.032</td>
<td>0.032</td>
<td>0.032</td>
</tr>
<tr>
<td>$H_{N_2}$(-)$^d$</td>
<td>0.016</td>
<td>0.016</td>
<td>0.016</td>
</tr>
<tr>
<td>$H_{Ar}$(-)$^d$</td>
<td>0.035</td>
<td>0.035</td>
<td>0.035</td>
</tr>
</tbody>
</table>

$^a$ $c_{gO_2}$, $c_{gN_2}$, $c_{gAr}$, $c_{O_2}^e$, $c_{N_2}^e$, $c_{Ar}^e$, $Q_g$ are outputs for all simulation sets

$^b$ Each experiment had a unique input within the reported range. For exact input values by experiment see Table G. 1.

$^c$ Concentrations are methane for the depleted influent simulations

$^d$ from Sander (2015)

Second, the model was used to conduct simulations to estimate aqueous and gas phase concentrations for hypothetical conditions using either: i) the range of $K_L$ values from the experiments (the $K_L$ calculated for each experiment was averaged between triplicate experiments conducted under similar conditions) and aqueous flow rates of 0.001-275 mL/min to predict the dissolved oxygen, nitrogen, and argon gases responses, or ii) a single $K_L$ value and a range of water flow rates along with a gas flow rate of 0.01 m$^3$/day and a range of influent water compositions. This lower gas flow rate represents the lower limit of reported SCVF rates (Alberta Energy Regulator, 2021a; Nowamooz et al., 2015) and the varying water compositions represent depleted concentrations of background dissolved gases. Depleted influent nitrogen concentrations were reported as a fraction of the total gas pressure in the influent water ($f$):
For the depleted influent simulations, oxygen concentrations were set to 0 mg/L and nitrogen concentrations were calculated such that $f$ ranged from 1 to 0.4. In this second set of simulations, trends for argon can be interpreted as being representative of trends for methane because their Henry’s coefficients are equal. If expressed in mol/L, the predicted concentrations of argon and methane would be the same. If expressed in mg/L, the argon concentrations in mg/L can be scaled by a factor of 0.4 to estimate the methane concentrations.

### 2.3 Results and Discussion

#### 2.3.1 Gas Migration and Saturations

Gas injection into the 3040 and 4060 sand packs generated branched and pooled source architectures, respectively. An example of each is shown in Figure 2.4 at various stages throughout the experiment. Areas of higher gas saturation are highlighted in red, indicating pooled gas structures ($S_g > S_{gr}$) and areas of lower gas saturations are highlighted in blue, indicating ganglia gas structures ($S_g \leq S_{gr}$).

Figure 2.4a and Figure 2.4e show the gas distributions when gas first breaks through the surface of the sand at the start of the active gas leak. The 3040 pack (Figure 2.4a) shows branched or finger-like gas migration patterns as gas invades larger pore spaces and higher permeability pathways to reach the surface (Geistlinger et al., 2006; Ji et al., 1993; Molofsky et al., 2021; Stöhr & Khalili, 2006). Gas migration is sensitive to small-scale heterogeneities as seen by the gas pools formed under the lower permeability (higher entry pressure) topset lamina lenses (Geistlinger et al., 2006; Glass et al., 2001; Ji et al., 1993; Tomlinson et al., 2003). In the 4060 pack (Figure 2.4e), pool heights required to exceed the higher entry pressures of the finer 40-60 sand were larger than in the 3040 pack (Glass et al., 2001). Gas pools backfilled following the finer grained foreset lamina in the cross beds and breakthrough occurred approximately 8 min after injection began. The
higher permeability contrast caused a delay in the initial gas breakthrough at surface compared to the branched source architectures where breakthrough occurred within 1 min of initial gas injection.

Figure 2.4b and Figure 2.4f show gas saturations after prolonged gas injections (hours after gas injection started). Small-scale heterogeneities and channel snap-off caused gas migration pathways to shift at early time, finding the easiest pathways to surface (Geistlinger et al., 2006). These shifts at early time are most obvious in the 3040 pack by the formation of a third gas finger on the upper left side of the gas envelope. At later time, a steady state gas migration pathway was established which remained constant for the remainder of the experiment. The gas migration pathways did not change significantly in the 4060 pack.

A total of 6.1-12.2 mL and 43.9-92.2 mL of gas was present in the sand pack at the end of the active gas leak (i.e., immediately before gas injection was stopped) in the 3040 and 4060 experiments, respectively. The experiments were classified by their gas source architectures using the GTP ratio (Table 2.1). The 3040 experiments resulted in the highest GTP ratios, with GTP > 1 in all but one experiment (0.73 in experiment 3040F-3). This indicates the bulk of the gas volume existed as ganglia during the active gas injection, which is consistent with observations of branched source architectures. Experiment 3040F-3 had a GTP ratio of 0.73 due to the formation of more gas pools at higher saturations under the capillary barriers. The GTP ratio for 3040F-3 was still larger than all 4060 GTP ratios and the gas saturation pattern was visually more similar to the branched source architectures than the pooled source architectures. GTP ratios for 4060 experiments were all less than 1, indicating the bulk gas volume existed as pools.

Figure 2.4c and Figure 2.4g show the gas saturations shortly after gas injection was stopped. Relaxation of gas branches and pools was evident as gas injection pressure decreased. Gas saturations were redistributed and decreased as buoyancy forces continued to drive gas movement in connected channels shortly after injection stopped, eventually forming trapped pools and ganglia (Elder & Benson, 1999; Stöhr & Khalili, 2006; Van De Ven et al., 2020; Van De Ven & Mumford, 2020c).
Figure 2.4d and Figure 2.4h show the gas saturations at later time following dissolution of the remaining trapped gas. Dissolution resulted in smaller gas pools and lower gas saturations. At the end of dissolution, 4.7-7.4 mL of gas remained in the branched source zones and 17.6-37.5 mL remained in the pooled source zones (i.e., a 31% and 54% reduction, respectively). GTP ratios increased for all experiments from active leak to post-repair states, indicating that pools transition to ganglia and ganglia are persistent during dissolution. It is expected that this would create an increase in gas-water interfacial area as dissolution continued.

**Figure 2.4**: Gas saturation maps at various stages throughout the active leak and post-repair stages. Panels show gas saturations at the initial gas injection (a and e), after prolonged gas injections (b and f), during relaxation (c and g), and at the end of post-repair dissolution (d and h) where t=0 when gas is first injected into the flow cell. One experiment (3040S-3 and 4060S-3) is shown as an example for each heterogeneity to demonstrate the differences in gas saturations for the branched and pooled architectures.

The evolution of macroscopic gas saturations during each stage of the experiments are also shown in Figure 2.5. Unlike the local gas saturations shown in Figure 2.4, the macroscopic gas saturations represent the total gas volume normalized to the total pore volume of the cell. Macroscopic gas saturations increased rapidly
during the initial gas injection at 2 pore volumes and remained steady during the active leak stage until gas injection was stopped at 7 pore volumes. The rapid decrease of gas saturations following repair was indicative of the relaxation period. Gas saturations then gradually decreased during post-repair as dissolution occurred. Higher macroscopic gas saturations occurred in the experiments with pooled source zones, however, in all cases gas saturations never reached zero during dissolution.

Figure 2.5: Macroscopic gas saturations by pore volume for each series of experiments. Red and blue colours represent fast (3.8 m/day) and slow (0.9 m/day) aqueous fluxes, respectively, and open and closed symbols refer to branched (3040) and pooled (4060) source zones, respectively. Branched source zone saturations are plotted with pooled source zone saturations for scale and every second data point is plotted for the pooled source architectures for clarity.

2.3.2 Background Dissolved Gas Response to Gas Injections

DO concentrations throughout each experiment are shown in Figure 2.6, and show: 1) a decrease in DO concentration from baseline to a steady depleted level during the active leak stage and 2) a return to baseline during the post-repair stage.
Figure 2.6: Dissolved oxygen concentrations measured in effluent water for branched (3040) and pooled (4060) heterogeneities at fast (3.8 m/day) and slow (0.9 m/day) aqueous fluxes during a baseline, active gas injection, and post-repair state. Every tenth data point is plotted for clarity. Error bars for data points are the size of or smaller than the symbol. In the cases that are larger, error bars are shown on one symbol of each stage of the experiment for clarity.

In all cases, DO concentrations decreased until they reached a depleted steady state, approximately 1-2 pore volumes following initial gas injection. This decrease in concentration occurred due to multi-component mass transfer at the gas-water interface. Argon gas dissolved into the aqueous phase while DO was simultaneously stripped (partitioned into the gas phase) consistent with responses measured in the field by Forde et al. (2019). Gas injection was maintained until a steady state was reached in the DO concentration (5 pore volumes). After 7 pore volumes, gas injection was stopped and DO concentrations began to return to baseline conditions. The pumped influent provided a continuous delivery of oxygen-rich water to the trapped gas interfaces, however, without a replenishment of injected gas, the argon was completely dissolved from the gas phase allowing the exchange of gases to stop and background dissolved gas concentrations to return to baseline conditions. Aqueous flow was maintained until the DO concentrations
returned to baseline concentrations (7 and 13 pore volumes for 3040 and 4060, respectively). Local (Figure 2.4d and Figure 2.4h) and macroscopic (Figure 2.5) analyses of gas saturations in the flow cell show that gas remained in the cell despite DO concentrations returning to baseline conditions. This suggests that background dissolved gases have replaced the argon gas to sustain these gas structures, consistent with observations from Forde et al. (2019), Van De Ven & Mumford (2020a), and Van De Ven & Mumford (2020b).

Figure 2.6 can also provide insight regarding the extent of mass transfer by looking at the change in DO concentrations from baseline conditions to the depleted steady state during the active leak stage. Cases with a large change in DO concentrations suggest more stripping of background dissolved gases from the influent water, which has implications regarding the detectability of change in background gases in field applications. Pooled source architectures produced the largest change in DO concentrations from baseline to the depleted steady state (Table 2.3). This is best shown by comparing experiments of similar aqueous velocities. At fast aqueous velocities, the branched (3040F) and pooled (4060F) source zones resulted in an average DO decrease of 3.0 mg/L and 4.5 mg/L, respectively. Similarly, at slower aqueous velocities the branched (3040S) and pooled (4060S) source zones results in an average DO decrease of 4.4 mg/L and 5.5 mg/L, respectively. Pooled structures allow for more stripping of dissolved gases likely due to increased contact area between the gas and aqueous phases over a longer path length (Van De Ven & Mumford, 2020c). The results shown in Figure 2.6 indicate that the source architecture classification (branched or pooled) is more important than the exact geometry of the gas pathway in dictating the detectability of changes in background dissolved gas concentrations. For example, the gas migration pathways observed in the 3040S experiments were all unique (Figure C. 5), yet all were classified as branched architectures (GTP > 1) and the three DO concentration curve triplicates are similar.

The detectability of the DO concentration change was also influenced by the aqueous velocity. In the branched source architectures, changes in DO concentrations were 1.4 times greater at the slower aqueous
velocity (3040S) than at the fast aqueous velocity (3040F). Similarly, in the pooled source architectures, changes in DO concentrations were 1.2 times greater at the slower aqueous velocity (4060S) than at the fast aqueous velocity (4060F). Slower aqueous velocities allow for more efficient mass transfer between the gas and aqueous phases due to increased contact time between the aqueous and gas phases. This sensitivity to aqueous velocity shows that mass transfer was rate limited in these experiments when evaluated at the scale of this flow cell. Rate-limited mass transfer occurred despite aqueous velocities being less than 4 m/day, which are conditions where the local equilibrium assumption (LEA) for mass transfer has been previously shown to provide good estimates of multi-component mass transfer from trapped gas in one-dimensional experiments (Geistlinger et al., 2005). Therefore, the detectability of changes in background dissolved gases in the field will be affected by heterogeneities in the subsurface and may be affected by the groundwater flow rate.

### Table 2.3: Summary of changes in DO concentrations.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Source Architecture</th>
<th>Average Concentrations (mg/L)</th>
<th>Change in DO Concentration (mg/L)</th>
<th>Average $K_L$ (m³/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Baseline⁴</td>
<td>Active Leak (Steady State)⁴</td>
<td></td>
</tr>
<tr>
<td>3040F</td>
<td>Branched</td>
<td>8.6 ± 0.06</td>
<td>5.5 ± 0.46</td>
<td>3.0 ± 0.46</td>
</tr>
<tr>
<td>3040S</td>
<td>Branched</td>
<td>8.8 ± 0.02</td>
<td>4.4 ± 0.46</td>
<td>4.4 ± 0.46</td>
</tr>
<tr>
<td>4060F</td>
<td>Pooled</td>
<td>8.6 ± 0.06</td>
<td>4.1 ± 0.28</td>
<td>4.5 ± 0.29</td>
</tr>
<tr>
<td>4060S</td>
<td>Pooled</td>
<td>8.9 ± 0.08</td>
<td>3.4 ± 0.14</td>
<td>5.5 ± 0.16</td>
</tr>
</tbody>
</table>

*average of all triplicates for each experimental condition

2.3.3 Steady-State Model

The impacts of heterogeneity and groundwater velocity on the detectability of a change in background dissolved gas concentration is further supported by results from the steady-state model, which focuses only on the active leak stage. Figure 2.7a shows the predicted change in DO concentrations over a range of Darcy flux rates using the average $K_L$ values fit to each of the four experimental conditions. Measured concentrations of oxygen in the influent and effluent water were input into the steady-state model to calculate a $K_L$ for each experiment (total of 12 $K_L$ values). One $K_L$ value (Table 2.3) was determined for each experimental condition by taking an average of the three $K_L$ values calculated for each set of triplicates.
Each of the curves in Figure 2.7 assumes that $K_L$ does not change with a change in Darcy flux, and represent a range of behaviour over possible $K_L$ values rather than a single prediction for any specific source. Future work will likely require the incorporation of expressions that account for changes in $K_L$ with changes in flux (e.g., Imhoff et al., 1998; Miller et al., 1990; Nambi & Powers, 2003; Powers et al., 1994; Saba & Illangasekare, 2000). Using these average mass transfer rate coefficients as a model input, the aqueous flow rate was adjusted to generate each curve in Figure 2.7. The definition for the change in concentration used here was the difference between the initial concentration of dissolved gas in the influent and the final concentration of dissolved gas in the effluent during the active leak steady state. Therefore, the change in argon concentration is represented as a negative change because it moves in the opposite direction of the oxygen and nitrogen, starting with no argon in the influent water and reaching elevated concentrations in the effluent. Each experimental condition has a unique curve indicating that both the source architecture and groundwater velocity influence the mass transfer between the aqueous and gas phases. The model is also useful to infer the methane and nitrogen concentrations that would be measured in the field from the argon and oxygen surrogates used in the laboratory experiments.

Treating argon as a surrogate for methane, the model predicts that as groundwater flow rates increase, the changes in dissolved oxygen, nitrogen, and methane approach zero. The aqueous phase flows past the gas phase too quickly for the exchange of gases to occur, failing to dissolve methane from the gas phase and allowing the effluent water to remain high in background dissolved gases. That is, the detectability of changes in dissolved nitrogen decreases with increasing Darcy flux. Assuming that a 30% change in nitrogen from background conditions is detectable, then a monitoring point immediately down gradient of a source can detect a change at Darcy fluxes up to approximately 1 m/day. However, considering that monitoring points likely cannot be located directly near a source due to uncertainties in source identification, then dispersion will decrease that observed change causing it to only be detectable at lower Darcy fluxes. Below a Darcy flux of 0.1 m/day, the detectability is not sensitive to the Darcy flux and will depend predominantly on dispersion.
Figure 2.7: Changes in concentration from baseline to depleted steady-state concentrations under experimental conditions for a) oxygen, b) nitrogen, and c) argon over a range of Darcy fluxes. Open symbols and closed symbols represent 3040 and 4060 sand mixtures, and red and blue represent fast and slow fluxes, respectively. Solid and dashed lines represent model results. $K_L$ values in the legend are in m$^3$/min.

The detectability of changes in dissolved nitrogen is also impacted by the initial nitrogen content of the influent water (Figure 2.8). The change in dissolved nitrogen is proportional to the amount of nitrogen initially in the water. Therefore, if the fraction of nitrogen concentration is half of the concentration in equilibrium with the atmosphere, the concentration change is approximately half as well. This indicates that it may be harder to detect stray gas migration using background dissolved gases at sites with naturally depleted background gas conditions. The depleted nitrogen content of the influent water, however, does not significantly impact the change in dissolved argon concentrations (and, therefore, will not impact the change in dissolved methane concentrations at field sites). The system is dominated by high concentrations of argon gas at atmospheric conditions, therefore changes in nitrogen or oxygen concentrations in the influent water only cause minor variations (< 1%) in argon gas concentrations in the effluent. Gas injection rates would need to be much smaller than the lowest limit of reported SCVF rates (0.01 m$^3$/day) to see changes in argon concentrations with depleted influent background gas conditions.
Figure 2.8: Changes in dissolved gas concentrations from baseline to depleted steady-state concentrations under depleted influent conditions. In all cases, dissolved oxygen was set to 0 and nitrogen concentrations were calculated such that \( f \) varied from 0.4 to 1. A constant \( K_L = 6 \times 10^{-6} \) m\(^3\)/min was used, which was the average of the four \( K_L \) values used for the simulations in Figure 2.7. Argon concentrations can be scaled by a factor of 0.4 to predict methane concentrations expressed as mg/L.

2.4 Conclusions and Recommendations

Laboratory experiments tracking DO concentrations during and after a gas leak demonstrate that mass transfer between background dissolved gases and stray gas is influenced by both source architecture and groundwater flow rate. Pooled source architectures and slow aqueous velocities resulted in the most stripping of background dissolved gases, which resulted in a lower depleted steady state concentration during active gas injection and a higher detectability. These findings are supported by predictions from the steady-state model as each experimental condition resulted in a unique \( K_L \). The steady-state model also shows that during the active leak, the system is rate-limited, and mass transfer kinetics cannot be ignored even at the slow aqueous velocities used in these experiments. This has implications for future modeling.
that may be developed for use at the field scale. Finally, the model predicts that depleted background gas influent conditions will lower the detectability of dissolved nitrogen but will not impact the dissolved methane response at gas flow rates near the lower limit of reported SCVF, in the absence of methane degradation. Future work should include analyzing the transient component of the post-repair background dissolved gas response, focusing on the changes in $K_L$ with dissolution and time. Additionally, consideration of scenarios where the detectability may be diminished, such as flow bypassing and dispersion, should be reviewed.

2.5 References


CCA. (2014). Environmental impacts of shale gas extraction in Canada.


Chapter 3
Gas-water mass transfer: Investigating the impacts of mass transfer rate coefficients and multi-component dissolved gases on gas dissolution

3.1 Introduction

Gases that enter shallow aquifers from deeper formations can persist and generate long-term source zones for groundwater contamination (Roy et al., 2016). Stray methane gas from leaking natural gas wells due to poor well integrity is one example of gas contamination in shallow aquifers (Dusseault & Jackson, 2014; Moortgat et al., 2018; Nowamooz et al., 2015). As groundwater flows past contaminated zones, mass transfer occurs between the aqueous and non-aqueous (i.e., gas) phases (Fry et al., 1995; Geistlinger et al., 2005), which can negatively impact groundwater quality through changes in redox conditions and pH, and can mobilize dissolved metals (Cahill et al., 2018; Schout et al., 2018; Schwartz, 2015; Van Stempvoort et al., 2005; Vengosh et al., 2014). Monitoring and detection tools for leaking natural gas wells are highly dependent on surface and aqueous expressions (Alberta Energy Regulator, 2021; Bachu, 2017; McIntosh et al., 2019) which can be reduced or delayed by dissolution of stray gas, leading to a reduction in detection and monitoring reliability (Cahill et al., 2018; Schout et al., 2020). The persistence of trapped methane gas and the associated impacts on groundwater quality lie at the intersection of fundamental mass transfer concepts and stray gas migration modelling studies, both of which must be considered.

In the past, mass transfer studies have been conducted to investigate the fate of contaminants in groundwater for both non-aqueous phase liquid (NAPL) and gas contaminants, used to develop approaches for predicting the time required to deplete contaminant source zones to acceptable levels, and to understand how depletion behaviour changes as source zone mass is decreased (Kokkinaki et al., 2013; Parker & Park, 2004; Saba & Illangasekare, 2000; Zhu & Sykes, 2000). Researchers also study mass transfer to understand various remediation techniques that rely on effective contact area between aqueous and gas phases such as
bioremediation or air sparging (Fry et al., 1995; Geistlinger et al., 2005; Geller & Hunt, 1993; Holocher et al., 2003; Kokkinaki et al., 2013). Some of the fundamental gas-water mass transfer studies include single-component partitioning tracer tests investigating the retardation effects of trapped gas (Donaldson et al., 1997; Fry et al., 1995, 1996), experimental and modelling investigations on the multi-component nature of gas-water partitioning (Amos & Mayer, 2006a, 2006b; Cirpka & Kitanidis, 2001), and variable gas volume multi-component partitioning studies (Geistlinger et al., 2005; Holocher et al., 2003).

Modeling has also been used to study stray gas migration due to the complexity and high cost of conducting field experiments (Schout et al., 2020). Many numerical models have been used to study the migration of methane gas through high permeability conduits (Kissinger et al., 2013; Nowamooz et al., 2015), mobilization of dissolved metals due to free-phase gas (Reagan et al., 2015), and impacts of multiphase flow parameters on gas flow rates and volumes that reach shallow groundwater from producing wells (Klazinga et al., 2019; Rice et al., 2018). Other stray gas numerical models have considered the transport and extent of dissolved methane plumes in the subsurface from a leaking geothermal well (D’Aniello et al., 2020) and illustrated the impacts of preferential pathways, injection rates, and heterogeneities on gas migration and dissolved methane plumes (Moortgat et al., 2018). Despite the range of modeling studies that have investigated stray gas migration, and despite the potential impacts to groundwater quality associated with the mass transfer of stray gas to the aqueous phase, only two studies have included methane dissolution in their models (Roy et al., 2016; Schout et al., 2020).

Roy et al. (2016) conducted a numerical study investigating the effects of methane leakage duration, gas inflow rate, and biodegradation processes on dissolved methane concentrations in confined and unconfined aquifers during an active gas leak and during post-repair. The simulations were performed using a two-phase (liquid, gas), multi-component transport model coupled with a biodegradation module (Roy et al., 2016). Although the model used in their study was a multi-component model, only one gas component (methane) was considered, omitting any background dissolved gases from their analysis. Their study was
largely focused on the attenuation of methane due to biodegradation, however, some nonreactive simulations were conducted in the confined aquifer to represent the most conservative dissolved methane attenuation estimates. Their study showed that nonreactive simulations with gas inflow rates of 0.02 and 0.2 m$^3$/day for a 2-year leak period required 5.5 and 17 years, respectively, for dissolution to reduce dissolved methane concentrations below the threshold level of 10 mg/L set by the US Office of the Interior (Nowamooz et al., 2015; Roy et al., 2016). Cases with gas inflow rates greater than 2 m$^3$/day for a 2-year and 4-year leak period still exceeded threshold levels after the 25-year simulation period. Short-term gas leaks (leak duration of 0.5 years) reached threshold levels by 19 years. Cases where biodegradation was considered required generally shorter timeframes to reach threshold limits (Roy et al., 2016). This study showed that methane can be retained in the subsurface for significant periods of time following well repair due to dissolution.

Schout et al. (2020) also conducted a series of numerical simulations to investigate the impact of various system parameters on methane dissolution. The study was carried out using a two-phase (liquid, gas), two-component (water, methane) model simulating gas and dissolved methane plumes during a continuous methane injection in both homogeneous and heterogeneous domains. Multiple parameters were varied (e.g., residual gas saturation, groundwater velocity, sediment properties) to test the sensitivity of gas migration extent and dissolved plume transport. Their study showed that in some simulations (e.g., those with fine sand media, very fast aqueous velocity, high residual gas saturation) gas did not reach the surface and generated significant dissolved methane plumes (Schout et al., 2020). This study highlighted the impact of dissolution on surface and aqueous expressions at various time scales which has implications for monitoring and detection. Unlike Roy et al. (2016), this study only investigated dissolution during a gas leak and not after the leak had been stopped (repaired), thereby providing limited insight regarding the persistence of trapped gas over time.
Importantly, both Roy et al. (2016) and Schout et al. (2020) assumed that the leaking gas was pure methane, and no gas-water exchange of other dissolved gases was considered, even though it has been shown in the context of applications other than stray gas migration that multiple dissolved gas components can affect dissolved gas concentrations due to competition for space in the gas phase (Amos & Mayer, 2006a; Cirpka & Kitanidis, 2001). Additionally, both models by Roy et al. (2016) and Schout et al. (2020), were run under the local equilibrium assumption (LEA), such that mass transfer kinetics were ignored. The model used by Roy et al. (2016) had a kinetic mass transfer term included in the governing equation, however, a sufficiently high kinetic term was applied so that methane dissolution occurred at equilibrium. LEA is dependent on scale and aqueous velocity, and is typically applied at slow aqueous flow rates. Although mass transfer at the local (interface, pore) scale tends to be at or near equilibrium, rate limited expressions may be required at the field scale (Parker & Park, 2004). Roy et al. (2016) used a 3D model domain 250 m × 100 m × 25 m consisting of 204,309 elements (average grid size of 1.8 m × 1.6 m ×1.1 m) with finer discretization near the well and at the top of the aquifer while Schout et al. (2020) used a grid size of 0.5 m × 0.5 m × 0.5 m. The application of a rate-limited mass transfer expression requires the selection (or calculation) of a mass transfer rate coefficient.

Mass transfer rate coefficients are commonly computed using Sherwood correlations, which relate modified Sherwood numbers to aqueous flow rates, non-wetting saturations, and empirical fitting parameters (Kokkinaki et al., 2013; Saba & Illangasekare, 2000; Zhu & Sykes, 2000). Mass transfer rate coefficients are used to avoid quantifying the interfacial area (IFA) between the non-wetting and wetting phases, because the IFA is difficult to quantify with certainty due to the complexity of porous media heterogeneities and the transient nature of IFA with time as non-aqueous mass is removed (Geller & Hunt, 1993; Imhoff et al., 1994; Miller et al., 1990; Nambi & Powers, 2003; Powers et al., 1994; Saba & Illangasekare, 2000; Zhu & Sykes, 2000). Many studies have been conducted to develop Sherwood correlations for NAPL-water experiments in 1D columns (Imhoff et al., 1994; Miller et al., 1990; Powers et al., 1994) or 2D flow cell experiments (Nambi & Powers, 2003; Saba & Illangasekare, 2000). These studies resulted in a wide range
of unique fitting parameters. Studies further investigating these Sherwood models indicate that they are highly system dependent and have a poor predictive capacity for experimental conditions that differ from those originally used to derive each model (Kokkinaki et al., 2013; Nambi & Powers, 2003; Zhu & Sykes, 2000). Similar correlations have been developed for field scale models and are also site specific (Parker & Park, 2004). Few studies have investigated the applicability of Sherwood correlations in gas-water systems. Geistlinger et al. (2005) applied a previously developed Sherwood correlation to 1D, homogeneous gas injection and dissolution experiments, however, a Sherwood correlation in a 2D, heterogeneous gas-water system has not been investigated.

The objectives of this study were to 1) develop a Sherwood correlation suitable for gas dissolution from a heterogeneously distributed gas source, 2) compare gas-water Sherwood parameters to those from previously developed NAPL-water Sherwood models and 3) investigate the impact of the mass transfer rate coefficient and inclusion of multiple dissolved gas components on the dissolution of trapped gas. To achieve these objectives a Sherwood model was developed for a series of intermediate-scale laboratory gas injection and dissolution experiments outlined in Chapter 2 and was compared to popular Sherwood models from the NAPL literature. A simple single-cell kinetic model that accounted for the source gas and background dissolved gases was then developed to simulate the dissolution of trapped gas (representative of post-repair conditions) in the same laboratory experiments. Simulations were run with a constant mass transfer rate coefficient and a transient mass transfer rate coefficient and were compared to measured gas saturations and dissolved gas concentrations. Additional simulations were conducted at various background dissolved gas conditions to show the differences in gas saturation and dissolved gas predictions for single- and multi-component gas scenarios.
3.2 Background

3.2.1 Gas Injection Experiments

A series of intermediate-scale laboratory experiments were conducted to measure gas saturations and dissolved gas concentrations during and following a prolonged gas injection. The experiments are described in detail in Chapter 2 and are summarized here. Argon gas (used as a surrogate for methane gas) was injected in the bottom of a quasi 2D flow cell (40 cm × 39.6 cm × 1.15 cm) packed with saturated sand mixtures deposited in cross-bedded formations to simulate an active gas leak. Gas flow was then shut off to simulate a successful well repair. Water was pumped through the cell at a continuous flow rate during the active gas leak and post-repair stages. Dissolved oxygen (DO) was measured in the effluent water to track the changes in background dissolved gases and light transmission methods were used to quantify gas saturations throughout the duration of the experiment. Experiments were conducted in two different sand packs, either a mixture of 20-30 and 30-40 or 20-30 and 40-60 (4:1 by mass) mesh size silica Accusand (Schroth et al., 1996), referred to by the finest grained material in the mixture, and at two different Darcy fluxes (3.8 m/day or 0.9 m/day) referred to as fast and slow, respectively. Each combination of experimental conditions was run in triplicate, resulting in a total of 12 experiments (see Chapter 2, Table 2.1).

Results from the previous study (Chapter 2) showed that as argon gas was injected into the flow cell, DO concentrations decreased until a new depleted steady state was reached at approximately 1-2 pore volumes after initial gas injection (Figure 3.1a). Changes in DO concentrations from initial conditions to depleted steady state were largest in experiments with pooled source architectures (4060) and at slower groundwater flow rates. When the gas was shut off, DO concentrations rebounded back to initial baseline conditions over time. The timing of the post-repair rebound was longer in experiments with pooled source architectures than branched source architectures. Measured gas saturations (Figure 3.1b) increased rapidly during initial gas injection and remained at a steady state throughout the active leak stage. When the gas injection was stopped,
gas saturations decreased rapidly, but not completely, due to relaxation and gradually decreased over time due to dissolution, but never reached zero.

Figure 3.1: Measured a) DO concentrations in the effluent water and b) gas saturations for one 4060F experiment during the baseline, active gas leak, and post-repair stages. Every 10th data point (a) and every second data point (b) is plotted for clarity. The solid black line and dashed black line in a) indicate the initial and depleted DO concentrations used in the steady-state model (SSM), respectively, to determine $K_L$. The black circle in b) identifies the initial gas saturation used in the kinetic model.

3.2.2 Steady-State Model

A simple steady-state model was developed to predict the aqueous and gas concentrations of three components ($O_2$, $N_2$, and Ar in the experiments) and estimate the response of background dissolved gases during an active gas leak for a range of possible site conditions. The steady-state model is described in detail
in Chapter 2. The model treats the flow cell as one grid block and tracks the aqueous and gas phases for each of the components of interest into and out of the cell. The governing equations for the aqueous and gas phases are:

\[
\frac{dm_{wj}}{dt} = Q_w c_{wj}^i - Q_w c_{wj} + k_w A_{gw} (c_w^* - c_{wj}) \quad (3.1)
\]

\[
\frac{dm_{gj}}{dt} = Q_g c_{gj} - \dot{m}_{gj} - k_w A_{gw} (c_w^* - c_{wj}) \quad (3.2)
\]

where \textit{w} refers to the aqueous phase and \textit{g} refers to the gas phase, \textit{j} is the component of interest, \(dm/dt\) is the mass rate of change, \(Q_w\) is the aqueous flow rate, \(c_{wj}^i\) is the influent concentration, \(c_{wj}\) is the concentration in the aqueous phase, \(k_w\) is the mass transfer coefficient (L/T), \(A_{gw}\) is the interfacial area between the gas and water phases, \(c_w^*\) is the concentration at the gas-water interface, \(Q_g\) is the gas flow rate out of the cell, and \(\dot{m}_{gj}\) is the mass flow rate of gas injected. The steady-state model assumes there is no change in the total mass for the gas and aqueous phases \((dm/dt = 0)\) resulting in:

\[
c_{wj} Q_w = c_{wj} Q_w - K_L (c_w^* - c_{wj}) \quad (3.3)
\]

\[
\dot{m}_{gj} = c_{gj} Q_g - K_L (c_w^* - c_{wj}) \quad (3.4)
\]

where \(K_L\) is the lumped mass transfer rate coefficient (L^3/T). Eq. 3.3 and 3.4 are coupled using Henry’s Law and Dalton’s Law, resulting in a system of 10 equations solving for 10 unknowns.

The model was first used to determine \(K_L\) for each set of experimental conditions, based on the steady-state DO concentration (Figure 3.1a) in each of the 12 experiments presented in Chapter 2. The model predicted a unique \(K_L\) for each of the 12 experiments, indicating the mass transfer is rate-limited even at slow aqueous fluxes, despite flow rates being lower than those shown to maintain LEA (4 m/day) in previous 1D column experiments (Geistlinger et al., 2005).
3.2.3 Sherwood and Upscaled Mass Transfer Correlation Theory

Mass transfer can be described as a function of a driving force and an IFA:

\[ J = \frac{1}{A_{gw}} \frac{dm}{dt} = k_w(c_w^* - c_w) \]  

(3.5)

where \( J \) is the mass flux from a gas to liquid phase (Miller et al., 1990). Mass transfer is highly dependent on the IFA between aqueous and non-aqueous phases, however, the IFA is difficult to quantify with accuracy because it changes with time as the non-aqueous phase dissolves and due to source architecture, which causes some areas of the non-aqueous phase to be more accessible to flowing water than others (Miller et al., 1990; Zhu & Sykes, 2000). Researchers commonly use the lumped mass transfer rate coefficient \( (K_L) \), which groups together the mass transfer coefficient \( (k_w) \) and the IFA \( (A_{gw}) \) to circumvent this challenge (Kokkinaki et al., 2013; Miller et al., 1990; Saba & Illangasekare, 2000; Zhu & Sykes, 2000). The mass transfer rate coefficient can also be combined with a specific interfacial area (i.e., interfacial area per unit volume), referred to here as \( K_{sh} \), to give a lumped mass transfer rate coefficient with units of 1/T. That mass transfer rate coefficient is often determined using Sherwood expressions (Kokkinaki et al., 2013). Although the specific terms included in Sherwood expressions can vary between studies, they take the general form:

\[ Sh' = \frac{K_{sh} d_{50}^2}{D_m} = b \cdot Re^c \cdot S_{NW}^d \]  

(3.6)

where \( d_{50} \) is the median particle diameter, \( D_m \) is the contaminant molecular diffusion constant in water, \( Re \) is the Reynolds number, \( S_{NW} \) is the saturation of the non-wetting phase, \( b, c, d \) are empirical fitting coefficients, and \( K_{sh} \) is the mass transfer rate coefficient (1/T) \( (K_{sh} = K_L/nV_T S_w) \) where \( n \) is the porosity, \( V_T \) is the total volume, and \( S_w \) is the water saturation (Kokkinaki et al., 2013). The conversion from \( K_{sh} \) to \( K_L \) is based on the volume of porous media because mass transfer is dependent on the surface area between
aqueous and non-aqueous fluids. Eq. 3.6 is used to determine $K^{Sh}$ by fitting the empirical coefficients $(b, c, d)$ to a measured dataset, which can then be transformed to $K_L$ and used in Eq. 3.5 (given $K_L = k_w A_{gw}$) to determine the mass flux of the non-wetting phase. The expression in Eq. 3.6 highlights the influence of the non-wetting phase saturation ($S_{NW}$) and hydrodynamics ($Re$) of the system on the empirical correlation (Kokkinaki et al., 2013). Sherwood correlations in the literature have been primarily developed for NAPL-water systems under various experimental conditions (Imhoff et al., 1994; Miller et al., 1990; Nambi & Powers, 2003; Powers et al., 1994; Saba & Illangasekare, 2000). However, each model exhibits their own unique fitting parameter values specific to the experimental conditions under which the models were developed, suggesting Sherwood models are system specific (Kokkinaki et al., 2013).

At the field scale, mass transfer kinetics are expressed using an upscaled mass transfer coefficient, which averages mass transfer over a larger domain (Christ et al., 2006). Upscaled mass transfer coefficients commonly incorporate effective field parameters, making them less computationally intensive and easier to implement than local scale techniques (Christ et al., 2006; Parker & Park, 2004). Analogous expressions to local-scale Sherwood correlations have been developed for field-scale applications:

$$K_{eff} = \beta_0 \left( \frac{q}{K_s} \right)^{\beta_1} \left( \frac{m}{m_o} \right)^{\beta_2}$$

(3.7)

where $K_{eff}$ is the effective upscaled mass transfer rate coefficient (1/T), $q$ is the Darcy flux, $K_s$ is the saturated hydraulic conductivity, $m$ is the mass of the non-wetting phase in the source zone, $m_o$ is the initial mass of the non-wetting phase in the source zone, and $\beta_0, \beta_1, \beta_2$ are empirical fitting parameters (Parker & Park, 2004). Eq. 3.7 is dependent on mass ($m/m_o$), which can be thought of as a replacement for saturation, and hydrodynamics ($q/K_s$) and has three fitting parameters ($\beta_0, \beta_1, \beta_2$) similar to Eq. 3.6. $K_{eff}$ can then be transformed to $K_L$ and used in Eq. 3.5 to calculate the mass flux of the non-wetting phase, assuming that the concentrations are evaluated at the same scale as $K_{eff}$. Similar to local-scale correlations, upscaled correlations have been shown to be highly site specific (Christ et al., 2006; Parker & Park, 2004).
3.3 Methods and Materials

3.3.1 Sherwood and Upscaled Mass Transfer Correlations

This study compares five Sherwood models by Miller et al. (1990), Imhoff et al. (1994), Powers et al. (1994), Saba and Illangasekare (2000), and Nambi and Powers (2003) and one upscaled mass transfer model by Parker and Park (2004). These six models were chosen for comparison as they are commonly discussed in the literature and follow similar functional forms. The fit parameters for these six models were also compared to coefficients fit directly to the gas injection and dissolution experimental data from Chapter 2.

To properly compare models, all expressions were transformed to be written as a function of Darcy flux and saturation of the non-wetting phase:

\[ K_{Sh}^{h} = b' \cdot q^{c} \cdot S_{NW}^{d} \]  
\[ K_{L}^{h} = K_{Sh}^{h} \cdot (nV_{T}S_{w}) \]

where \( b' \) is a constant calculated using fit parameters determined empirically by each previous study (Table 3.1) and experiment parameters (Table 3.2), and \( K_{L}^{h} \) is the lumped mass transfer rate coefficient (L^3/T) determined using the Sherwood expression in Eq. 3.8A.

Table 3.1: Summary of fit parameters reported in the literature for the five Sherwood models and the one upscaled mass transfer model.

<table>
<thead>
<tr>
<th>Model</th>
<th>Dimension</th>
<th>Fit Parameters</th>
<th>b</th>
<th>c</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miller et al. (1990)</td>
<td>1D</td>
<td></td>
<td>12</td>
<td>0.75</td>
<td>0.6</td>
</tr>
<tr>
<td>Imhoff et al. (1994)</td>
<td>1D</td>
<td></td>
<td>340</td>
<td>0.71</td>
<td>0.87</td>
</tr>
<tr>
<td>Powers et al. (1994)</td>
<td>1D</td>
<td></td>
<td>4.13</td>
<td>0.598</td>
<td>0.815</td>
</tr>
<tr>
<td>Saba and Illangasekare (2000)</td>
<td>2D</td>
<td></td>
<td>11.34</td>
<td>0.28</td>
<td>1.04</td>
</tr>
<tr>
<td>Nambi and Powers (2003)</td>
<td>2D</td>
<td></td>
<td>37.2</td>
<td>0.61</td>
<td>1.24</td>
</tr>
<tr>
<td>Parker and Park (2004)^a,b</td>
<td>3D</td>
<td></td>
<td>0.049</td>
<td>1</td>
<td>1.4</td>
</tr>
</tbody>
</table>

^a Parameters shown are those derived for the mixed source zone of the upscaled model including finger and pooled source architectures.

^b \( b, c, \) and \( d \) parameters for Parker and Park (2004) represent \( \beta_{o}, \beta_{1}, \beta_{2} \), respectively.
Table 3.2 Summary of model inputs used to determine $b'$ for the six mass transfer models when applied to the gas injection experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median grain size diameter (mm)$^a$</td>
<td>$d_{50}$</td>
<td>0.713</td>
</tr>
<tr>
<td>Medium sand grain diameter (mm)$^b$</td>
<td>$d_{m}$</td>
<td>0.500</td>
</tr>
<tr>
<td>Uniformity Index (-)$^c$</td>
<td>$U$</td>
<td>1.19</td>
</tr>
<tr>
<td>Molecular diffusion coefficient (cm$^2$/s)$^d$</td>
<td>$D_m$</td>
<td>$2.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Viscosity of water (Pa.s)$^d$</td>
<td>$\mu_w$</td>
<td>0.001</td>
</tr>
<tr>
<td>Density of water (kg/m$^3$)$^d$</td>
<td>$\rho_w$</td>
<td>998</td>
</tr>
<tr>
<td>Density of gas (kg/m$^3$)$^d$</td>
<td>$\rho_{NW}$</td>
<td>1.641</td>
</tr>
<tr>
<td>Porosity (-)$^a$</td>
<td>$n$</td>
<td>0.32</td>
</tr>
<tr>
<td>Non-wetting phase saturation (-)</td>
<td>$S_{NW}$</td>
<td>0.081</td>
</tr>
<tr>
<td>Tortuosity (-)$^e$</td>
<td>$\tau$</td>
<td>2</td>
</tr>
<tr>
<td>Length scale (cm)</td>
<td>$L \ or \ x$</td>
<td>39.6</td>
</tr>
<tr>
<td>Total cell volume (cm$^3$)</td>
<td>$V_T$</td>
<td>1566.6</td>
</tr>
<tr>
<td>Saturated hydraulic conductivity (cm$^2$/min)$^a$</td>
<td>$K_S$</td>
<td>15.02</td>
</tr>
</tbody>
</table>

$^a$ as defined by Schroth et al., (1996)
$^b$ as defined by Powers et al., (1994)
$^c$ calculated from Ohsumi & Horibe, (1984)
$^d$ at 20°C
$^e$ as defined by Saba and Illangasekare (2000)

The definition of $b'$ is unique to each model (Table 3.3), as each of the six mass transfer expressions has a slightly different form. To transform models into the form of Eq. 3.8A, where necessary, Reynolds expressions were modified to be expressed as a function of Darcy flux ($q = vn[1 - S_{NW}]$) where $v$ is the aqueous velocity, and volumetric fractions of the non-wetting phase ($\theta_{NW}$) were expressed as a saturation ($\theta_{NW} = n[1 - S_{NW}]$). It was assumed the non-wetting phase saturation was constant (i.e., the correlations were applied to the steady-state phase of the experiments from Chapter 2). In addition to the six mass transfer models, coefficients $b', c$, and $d$ were fit directly to the experimental gas data (Table 3.3). To determine the best-fit values of the fitting coefficients, a mass transfer rate coefficient was calculated for each of the 12 experiments conducted using Eq 3.8B. The estimated $K_{L}^{Sh}$ was compared to the $K_L$ values calculated in the steady-state model for each experiment (i.e., $K_L$ values determined by solving a system of equations based on Eq. 3.3 and 3.4 without considering Eq. 3.8A). The solver tool in Excel was used to drive the sum of squares of the difference between $K_L$ and $K_{L}^{Sh}$ to a minimum by adjusting the $b', c$, and $d$ coefficients.
Table 3.3: Summary of fit parameter values and the definition of $b'$ unique to each model.

<table>
<thead>
<tr>
<th>Model</th>
<th>$b'$ (m$^{-1}$)</th>
<th>Definition</th>
<th>Value</th>
<th>c (-)</th>
<th>d (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas experiments</td>
<td>-</td>
<td>-</td>
<td>11.2</td>
<td>0.85</td>
<td>0.43</td>
</tr>
<tr>
<td>Miller et al. (1990)</td>
<td>$\frac{bD_m}{d_{50}^2} \left( \frac{\mu_w}{\rho_w D_m} \right)^{0.5} \left( \frac{\rho_w d_{50}}{\mu_w n(1 - S_{NW})} \right)^c n^d$</td>
<td>188.3</td>
<td>0.75</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Imhoff et al. (1994)</td>
<td>$\frac{bD_m}{d_{50}^2} \left( \frac{d_{50}}{d_{50}} \right)^{-0.31} \left( \frac{\rho_w d_{50}}{\mu_w n(1 - S_{NW})} \right)^c n^d$</td>
<td>18.6</td>
<td>0.71</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>Powers et al. (1994)</td>
<td>$\frac{bD_m}{d_{50}^2} \left( \frac{d_{50}}{d_{m}} \right)^{0.673} \mu^{0.369} \left( \frac{\rho_w d_{50}}{\mu_w n(1 - S_{NW})} \right)^c \left( \frac{1}{S_{NW_o}} \right)^d$</td>
<td>18.8</td>
<td>0.598</td>
<td>0.815</td>
<td></td>
</tr>
<tr>
<td>Saba and Illangasekare (2000)</td>
<td>$\frac{bD_m}{d_{50}^2} \left( \frac{\mu_w}{\rho_w D_m} \right)^{0.33} \left( \frac{\rho_w d_{50}}{\mu_w n(1 - S_{NW})} \right)^c \left( \frac{d_{50}}{n \tau L} \right)^d$</td>
<td>0.0007</td>
<td>0.28</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>Nambi and Powers (2003)</td>
<td>$\frac{bD_m}{d_{50}^2} \left( \frac{\rho_w d_{50}}{\mu_w n(1 - S_{NW})} \right)^c$</td>
<td>17.7</td>
<td>0.61</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>Parker and Park (2004)$^a$</td>
<td>$b \left( \frac{1}{K_s} \right)^c \left( \frac{1}{S_{NW_o}} \right)^d$</td>
<td>$6.6 \times 10^4$</td>
<td>1</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Parameters shown are those derived for the mixed source zone including finger and pooled source architectures.

### 3.3.2 Kinetic Model

The steady-state model presented in Chapter 2 was extended to a kinetic model to predict the gas saturation and dissolved gas concentrations (O$_2$, N$_2$, and Ar in the experiments) over time during the post-repair phase. This model considers the dissolution of the non-wetting phase only during the post-repair stage, after the gas injection has stopped (i.e., the gas is immobile). The model treats the flow cell as one grid block and tracks the aqueous and gas phase for each component of interest into and out of the cell. The mass balance for the aqueous and gas phases are expressed using Eq. 3.1 and 3.2, respectively. Assuming trapped gas ($\dot{m}_g = 0$ and $Q_g = 0$) and treating the change in saturation as negligible over small time intervals:

\[(3.9)\]
\[ \frac{\partial c_{wj}}{\partial t} = \frac{Q_w}{V_T n S_w^t} \left( c_{wj}^i - c_{wj} \right) + \frac{K_L}{V_T n S_w^t} \left( c_{wj}^* - c_{wj} \right) \]

\[ \frac{\partial m_{gj}}{\partial t} = -K_L (c_{wj}^* - c_{wj}) \]  

(3.10)

where Eq. 3.9 and 3.10 were then evaluated explicitly as a first-order backward finite difference in time (t):

\[ c_{wj}^{t+1} = \Delta t \left[ \frac{Q_w}{V_T n S_w} \left( c_{wj}^i - c_{wj} \right) + K_L \left( c_{wj}^* - c_{wj} \right) \right] + c_{wj}^t \]  

(3.11)

\[ m_{gj}^{t+1} = -\Delta t K_L \left( c_{wj}^* - c_{wj} \right) + m_{gj}^t \]  

(3.12)

Using the ideal gas law:

\[ P_T V_g = \sum \frac{m_{gj}}{M_j} RT \]  

(3.13)

where \( P_T \) is the total pressure, \( V_g \) is the volume of gas \( (V_g = V_T n S_g) \), \( M_j \) is the molar mass of component \( j \), \( R \) is the ideal gas constant, and \( T \) is the temperature. The gas saturation was updated at each time step:

\[ S_g^{t+1} = \frac{\sum \left( \frac{m_{gj}}{M_j} \right)^{t+1} RT}{V_T n P_T} \]  

(3.14)

Concentrations in the gas phase and at the gas-water interface were also updated with each time step:

\[ c_{gj}^{t+1} = \frac{m_{gj}^{t+1}}{V_g} = \frac{m_{gj}^{t+1}}{V_T n S_g^{t+1}} \]  

(3.15)

\[ c_{wj}^{*t+1} = H_j c_{gj}^{t+1} \]  

(3.16)

where \( H \) is the Henry’s coefficient, unique for each component of interest (Sander, 2015).
At each time step the model calculates a \( c_w, c_w^*, c_g \) and \( m_g \) for each component of interest and a \( S_g \) and \( S_w \), given constant input values of \( H_j, P_T, R, T, \Delta t, V_T, n, \) and \( Q_w \). Initial inputs at \( t = 0 \) include \( c_{wO_2} \) (measured at the end of the active leak stage), \( c_{wN_2}, c_{wAr}, c_{wO_2}^*, c_{wN_2}^*, c_{wAr}^* \), \( c_{gO_2}, c_{gN_2}, \) \( c_{gAr} \) (output from the steady-state model), \( c_{wO_2}^i \) (measured at baseline conditions prior to gas injection), \( c_{wN_2}^i \) (determined from a lookup table at the experimental temperature and pressure), and \( c_{wAr}^i \) set to zero. Initial \( S_g \) is set to the gas saturation measured after gas relaxation and is used to calculate the initial gas volume \( (V_g) \). Various \( K_L \) values were used for different simulation conditions either directly calculated by the steady-state model or calculated using the Sherwood expressions developed using the gas experimental data (i.e., based on \( K_{LSh} \)). It was assumed dispersion was negligible for the kinetic model (Figure E. 1).

### 3.3.3 Kinetic Simulation Sets

Two sets of simulations were conducted using the kinetic model: 1) \( K_L \) sensitivity and 2) multi-component sensitivity. The first set of simulations compared dissolved argon concentration and gas saturation predictions using a constant \( K_L \) and a transient \( K_L \). The first simulations tested a constant \( K_L \) calculated by the steady-state model. The \( K_L \) used for each experimental condition was an average \( K_L \) for each set of triplicates. Additional simulations in the first set tested a transient \( K_{LSh} \) calculated as a function of saturation, using \( b', c, d \) coefficients fit to the experimental dataset (Eq. 3.8B). \( K_{LSh} \) was updated at each time step, using gas saturations calculated at the previous time step. The two conditions were used to simulate four of the experiments, with one test chosen from each set of triplicates as a representative sample. In total 8 simulations were conducted in the first set of simulations.

The second set of simulations included adjusting the influent conditions to demonstrate the difference in predicted total gas saturation and aqueous concentrations when considering a single- compared to a multi-component dissolved gas system. In some simulations, all background dissolved gases (\( N_2, O_2 \)) were removed from the system. That is, initial inputs, \( c_{wO_2}, c_{wN_2}, c_{wO_2}^*, c_{wN_2}^*, c_{gO_2}, c_{gN_2}, c_{gO_2}^i, c_{gN_2}^i \) and \( c_{wAr}^i \).
were all set to zero. Additional initial argon mass was added to the system to satisfy the total pressure constraint for the measured gas saturations. Using the newly calculated $c_{gAr}$, the $c_{wAr}$ and $c_{wAr^*}$ were also recalculated for initial inputs. For additional simulations in the second set, the influent conditions were set to include dissolved gas compositions of 80% N$_2$, 20% O$_2$, and no argon, similar to the first set of simulations. Initial inputs at $t = 0$ included $c_{wO_2}$ (measured at the end of the active leak stage), $c_{wN_2}$, $c_{wAr}$, $c_{wO_2^*}$, $c_{wAr^*}$, $c_{gO_2}$, $c_{gN_2}$, and $c_{gAr}$ (output from the steady-state model), $c_{wO_2^i}$ (measured at baseline conditions prior to gas injection), $c_{wN_2^i}$ (determined from a lookup table at the experiment temperature and pressure), and $c_{wAr^i}$ set to zero. A constant $K_L$ determined using the steady-state model was used for all simulations in the second set. The single- and multi-component conditions were applied to the four experiments, resulting in a total of 8 simulations in the second set of simulations.

3.4 Results and Discussion

3.4.1 Gas-Water Sherwood Correlation Compared to NAPL Literature

Fit coefficients ($b'$, $c$, $d$) for the newly fit gas model were compared to those from the six previously developed mass transfer models. The comparison is shown in Figure 3.2, organized according to the scale of the study used to determine the model parameters, where scale refers to the total volume of the experimental column, flow cell, or simulation domain used for each study. Models derived by 1D and 2D experiments are indicated by red and blue closed symbols, respectively, 3D simulations by black closed symbols, and gas experiments by open symbols. Figure 3.2 shows that all fitting parameters generally increased in value with increasing scale, causing all field-scale fitting parameters to be greater than those derived in the laboratory. The $b'$ coefficient (Figure 3.2a) for most of the laboratory experiments were within a similar range. Imhoff et al. (1994), Powers et al. (1994), Nambi and Powers (2003), and Gas Experiments (Chapter 2) all had a $b'$ coefficient on the same order of magnitude, ranging from 11.2 to 18.8 m$^{-1}$. The Miller et al. (1990) $b'$ coefficient was one order of magnitude larger than the other 1D laboratory experiments with a value of 188.3 m$^{-1}$. The final two models had $b'$ parameters significantly different than
the previous cluster, with the Saba and Illangasekare (2000) 2D experiment resulting in a much smaller $b'$ parameter of 0.0007 m$^{-1}$ and the Parker and Park (2004) simulation resulting in a much larger $b'$ parameter of $6.6 \times 10^4$ m$^{-1}$.

The $c$ coefficients (Figure 3.2b) showed similar trends to $b'$. Laboratory experiments by Miller et al. (1990), Imhoff et al. (1994), Powers et al. (1994), Nambi and Powers (2003) and Gas Experiments (Chapter 2) resulted in $c$ coefficients in the range of 0.6-0.85, the $c$ coefficient from Saba and Illangasekare (2003) was again much lower at 0.28, and the $c$ coefficient from Parker and Park (2004) was much higher at 1.

The $d$ coefficients (Figure 3.2c) are grouped in three clusters of data points. The 1D experiments by Miller et al. (1990), Imhoff et al. (1994), and Powers et al. (1994) ranged from 0.6-0.817, the 2D experiments were higher at 1.04 and 1.24 for Saba and Illangasekare (2000) and Nambi and Powers (2003), respectively, and the field-scale model was highest at a value of 1.4. The gas model resulted in a $d$ parameter below all reported values at 0.43.

The gas fit parameters are generally on the same order of magnitude as the NAPL model coefficients, indicating that coefficients fit to the gas experiments are more similar to the NAPL laboratory experiments than the upscaled field models. Discrepancies between model parameters may exist due to differences in experimental conditions (e.g., source architecture, non-wetting phase saturations, dimensionality, scale) (Kokkinaki et al., 2013; Nambi & Powers, 2003). However, it should be noted that parameters fit to the gas experiments are still unique from the NAPL models, which supports previous findings that Sherwood models are specific to the conditions under which they were derived.
3.4.2 Mass Transfer Rate Coefficient Sensitivity on Gas Dissolution

Kinetic model simulations were conducted to predict the gas saturations (Figure 3.3a, c, e, g) and DO concentrations (Figure 3.3b, d, f, h) during gas dissolution using two different approaches for the lumped mass transfer rate coefficient. The simulation was first run with a constant $K_L$ (orange solid line) determined by the steady-state model. This simulation was generally good at capturing the decrease in gas saturations in all experiments. The model predicted lower gas saturations than were measured at later time, generating an increasingly worse fit with time for all experiments. The second simulation used a transient $K_{LS}^{Sh}$ dependent on saturation (green dashed line). The transient $K_{LS}^{Sh}$ simulation predicted slightly higher gas saturations than the constant $K_L$ condition, but still underpredicted measured gas saturations at late time. The $K_{LS}^{Sh}$ did not present a considerably better fit to the measured gas saturations than the constant $K_L$ simulation for all experimental conditions. Similar to the saturation predictions, the constant $K_L$ and the transient $K_{LS}^{Sh}$ simulations resulted in similar DO concentration curves. For all experimental conditions both simulations underpredicted DO concentrations at early time, however, they captured the general increasing trend of the measured DO concentrations well. This shows that a transient $K_{LS}^{Sh}$ does not significantly
improve the predictions of gas saturation and dissolved gas concentration, suggesting a constant $K_L$ is likely sufficient for gas dissolution modelling. It is likely that this is possible because the overall changes in gas saturation are relatively small in comparison to the changes in NAPL source zone saturations in previous studies of rate-limited mass transfer. Despite discrepancies between simulated and measured DO concentrations and gas saturations, both $K_L$ approaches successfully simulated: 1) a return to a steady-state DO concentration after 5-6 pore volumes and 12-14 pore volumes for the 3040 and 4060 experiments, respectively, and 2) a non-zero gas saturation at the end of the experiment.

3.4.3 Multi-component Sensitivity on Gas Dissolution Modelling

Kinetic model simulations (Figure 3.4) were also used to compare predicted gas saturations (dashed lines) and dissolved concentrations (solid lines) in a single-component (blue) and a multi-component (orange) dissolved gas system. The first simulation was a single-component analysis, which assumed no background dissolved gases (N$_2$, O$_2$) in the water, leaving argon as the only component. These are directly analogous to previous modelling studies of stray gas dissolution that considered only methane. Gas saturations decreased linearly until the trapped gas dissolved completely. Dissolved argon concentrations appeared as a step-wise curve, remaining constant until the gas phase was extinguished, at which point the dissolved argon concentrations dropped to zero because the source of argon (gas bubbles) was depleted. Total extinction of gas saturations occurs because gas bubbles cannot exist if the sum of partial pressures in the gas phase are less than the total pressure (Cirpka & Kitanidis, 2001). There are no additional dissolved gases in the single-component simulations to maintain the total pressure, therefore as argon is dissolved the partial pressures in the gas phase becomes less than the total pressure constraint. The single-component model estimates argon removal from the porous media after 1.55, 1.06, 3.95, and 6.48 pore volumes for the 3040F, 3040S, 4060F, and 4060S experiments, respectively. This behaviour is similar to what would be expected under LEA conditions for dissolution in a single-component system, which suggests that the $K_L$ values determined from the experiments were relatively high.
Figure 3.3: Kinetic model simulations predicting gas saturations and DO concentrations during dissolution using a constant $K_L$ (orange solid line) and a transient $K_{L,sh}$ as a function of saturation (green dashed line) for the 3040F (a, b), 3040S (c, d), 4060F (e, f), and 4060S (g, h) experiments (open circles).
The second simulation was a multi-component analysis, including background dissolved gases (N\textsubscript{2}, O\textsubscript{2}) and argon. Gas saturations decreased initially, however, less rapidly than predicted by the single-component model and never reached a saturation of zero. Gas saturations reached a steady state, and were sustained even after the argon gas dissolved from the system. This is consistent with previous laboratory studies (Van De Ven & Mumford, 2020; Chapter 2) that showed that background dissolved gases can sustain gas saturations even after an injected gas is removed by dissolution.

![Graphs showing simulated gas saturations and dissolved argon concentrations](image)

**Figure 3.4:** Kinetic model simulations for a single-component (SC) (blue) and a multi-component (MC) (orange) dissolved gas system. Simulated gas saturations (dashed line) and dissolved argon concentrations (solid line) are shown by pore volume.

Dissolved argon concentrations also started decreasing at early time, with a much more gradual decline than predicted by the single-component model. This gradual dissolution behaviour caused argon concentrations to persist much longer. The multi-component model estimated that argon decreased to a concentration of
1.3 mg/L (approximately 2% of argon solubility and analogous to methane detection limits of 0.54 mg/L (Van De Ven & Mumford, 2020)) after 5.51, 5.21, 9.92, 18.91 pore volumes for the 3040F, 3040S, 4060F, and 4060S experiments, respectively.

The comparison between the single- and multi-component model shows that trapped gases, and the dissolution of the original source gas, will persist longer in the presence of background dissolved gases. Argon persistence was approximately 3.5, 4.9, 2.5 and 2.9 times longer in the 3040F, 3040S, 4060F and 4060S experiments, respectively, when multiple dissolved gases were considered. This has important implications for the investigation of sites impacted by stray gas migration and for simulations to assess the timeframe on which impacts from trapped gas may be expected to persist. Stray gas investigations should include measurement of background dissolved gas concentrations, including persistent and atmospheric gases such as nitrogen and argon. Any simulations of gas persistence should account for these background dissolved gases, as well as multiple components in the source gas. If not, then simulations will underpredict methane persistence and the timeframe of associated impacts to groundwater quality.

3.5 Conclusions and Recommendations

Using experimental data and the steady state model described in Chapter 2, Sherwood coefficients were fit to the gas-water system and compared to coefficients previously determined for five NAPL-water laboratory-scale models and one field-scale model. A simple kinetic model was then used to simulate post-repair dissolution of the same laboratory experiments, testing the sensitivity of various lumped mass transfer rate coefficient conditions and background dissolved gas conditions. Comparison between the Sherwood correlation fit parameters showed that the gas experiments resulted in fit parameters more similar to the correlations derived from NAPL laboratory studies than the field-scale simulations. The gas coefficients, however, were still unique, which supports previous findings that Sherwood models are highly system dependent. The kinetic model was then used to determine the sensitivity of methane persistence to changes in the mass transfer rate coefficients and the inclusion of multiple dissolved gas components. Results showed
that the transient $K_L^{\text{th}}$ simulations did not improve the fit to the experimental data compared to using a constant $K_L$, suggesting a constant $K_L$ is sufficient for dissolution modelling under these conditions. Most importantly, results showed that the multi-component simulations predicted sustained gas saturations and considerably longer (2.5-4.9 times) gas persistence compared to the single-component simulations, which predicted rapid extinction of gas saturations and short gas residence times. The single-component models underpredicted gas persistence in aquifers following a repair which has implications for risk assessment and post-repair aquifer recovery.

It is recommended that future gas dissolution models consider background dissolved gases instead of just the one gas component of interest. It is likely that most, if not all, stray gas contamination problems involve multiple gas components. This may include multiple components in the source (leaking) gas as well as various background dissolved gases that are naturally present in groundwater. Multi-component source gases are important for stray gas migration from leaking natural gas wells, where the gas can contain other hydrocarbon gases (e.g., ethane, propane, butane) along with methane, as well as for gases related to other subsurface energy applications including impurities in captured carbon dioxide (e.g., methane, sulfur dioxide, carbon monoxide) and cushion gas used for underground hydrogen storage (e.g., nitrogen, carbon dioxide, methane). Any simulations of persistence associated with leaks of these gases to shallow groundwater should also account for the effects of gas components and background dissolved gases on mass transfer.

### 3.6 References


Chapter 4

Conclusions and Recommendations

4.1 Summary and Conclusions

Stray gas migration from leaking natural gas wells can cause changes to groundwater quality, create explosion and asphyxiation hazards, and contribute to greenhouse gas emissions. Leaks can occur in producing, decommissioned, and abandoned wells, creating a potentially ongoing problem even after gas production has been suspended. It is necessary to understand the interactions between methane gas and the background dissolved gases naturally occurring in the groundwater to improve monitoring tools and understand aquifer recovery times post-repair due to dissolution.

Intermediate-scale laboratory experiments were used to investigate the changes in background dissolved gases during an active leak and post-repair scenario in pooled- and finger-dominated source architectures and at fast and slow aqueous velocities. Measurements of dissolved oxygen (DO) showed that during an active gas leak, background dissolved gases were stripped from the water resulting in a drop in DO concentration until a steady state was reached. Pooled source architectures and slow aqueous flow rates resulted in more stripping of background dissolved gases from the water during an active gas leak, resulting in a higher detectability of changes in background dissolved gases. Detectability was also shown to be controlled by the general source architecture classification (i.e., pools vs. fingers), not the exact geometry of gas pathways. This was shown by triplicate experiments that resulted in similar dissolved gas concentration curves created by dissolution from different migration pathways. A simple one-grid block steady-state model was created to predict the mass transfer rate coefficients for each experimental condition and the change in background dissolved gases from baseline to depleted steady state at conditions different than those tested in the laboratory. The model predicted unique mass transfer rate coefficients for each experiment conducted showing that all experiments were rate-limited, even those that were conducted at aqueous velocities slower than LEA thresholds reported previously for 1D experiments. In a 2D system,
LEA thresholds may be lower than previously reported in the literature. The steady-state model was also used to predict changes in background dissolved gases at depleted influent conditions (lower background dissolved gas concentrations). These simulations showed that background dissolved gas detectability is proportional to the quantity of dissolved gases initially in the groundwater. Groundwater with higher initial background dissolved gas concentrations will result in greater changes in dissolved gases (higher detectability) than groundwater with low initial background dissolved gas concentrations. Due to the large quantity of argon gas injected in these experiments (as a surrogate for methane), argon concentrations were relatively unchanged with depleted background gas conditions. This indicates that it may be harder to detect stray gas using background dissolved gases at sites with naturally depleted background gas conditions.

During the post-repair stage (after gas injection was stopped), background dissolved gas concentrations rebounded back to initial baseline conditions as the source gas was dissolved. Experimental results showed that pooled source architectures required more time to rebound to initial conditions than the fingered source architectures. Gas saturations persisted in the cell despite background dissolved gas concentrations having returned to baseline conditions indicating that background dissolved gases partitioned into the gas phase to sustain gas saturations. A simple one-grid block kinetic dissolution model was developed to simulate the post-repair dissolution of the trapped gas. The model predicted dissolved gas concentrations and gas saturations and was compared to measured experimental data. A Sherwood correlation was developed for the gas injection experiments and compared to the local and upscaled Sherwood correlations developed in the NAPL literature. The Sherwood correlation for the gas experiments was most similar to the NAPL Sherwood correlations developed at the laboratory scale than the field scale but were still unique, supporting previous findings that Sherwood correlations are highly system specific. Kinetic dissolution simulations were then conducted using a constant mass transfer rate coefficient (determined from the steady-state model) and a transient mass transfer coefficient (determined using the gas-water Sherwood correlation). Predicted gas saturations and dissolved gas concentrations were compared to measured values and showed that model predictions were generally good at capturing the trends of the measured data. However, the fit was not
improved using the transient mass transfer rate coefficient, indicating that a constant mass transfer rate coefficient is likely sufficient for gas dissolution modelling under conditions similar to the experiments. The kinetic model was then used to simulate gas dissolution in a single-component dissolved gas scenario (only argon gas) and a multi-component dissolved gas scenario (argon, nitrogen and oxygen). The multi-component simulation resulted in gas persistence 2.5-4.9 times longer than in the single-component simulation. The multi-component simulation was also able to capture sustained gas saturations, whereas the gas saturations in the single-component model extinguished to zero rapidly. This highlights the importance of including multiple dissolved gases in dissolution modelling, even in cases with a single component source gas, to prevent underestimations of contaminant retention times.

4.2 Recommendations for Future Work

This study highlighted the interaction between background dissolved gases and stray methane gas. Additional insights may be gained through the following future work:

1. Increase the scale (field-scale) and dimensionality (3D) of the study to investigate the impacts of flow bypassing and dispersion on background dissolved gas detectability. Due to the 2D nature of the flow cell used in these experiments, flow bypassing was not included in the investigations. However, it is possible that flow bypassing and dispersion could generate background dissolved gas signals that are not indicative of the true nature of gas migration occurring in the subsurface. Dissolved gas signals may be weakened or diluted giving the impression that there is no stray gas present in the subsurface despite a leak occurring. This could potentially create dissolved gas signals that are not as clear as those presented in the laboratory experiments and may be a limitation for using dissolved background gases at the field scale. Field-scale investigations will be useful to test these findings in an environment less controlled than a laboratory setting.

2. Include background dissolved gases, like nitrogen, in baseline site characterization. When collecting groundwater samples prior to production and/or prior to well repairs, it is recommended that
background dissolved gases be included in the dissolved gas analysis in addition to dissolved methane. This additional information can be used in combination with other developed site investigation techniques to build a conceptual model of the stray gas conditions of a field site and may be used as a potential indicator for successful well repairs.

3. Include multiple dissolved gas components in future stray gas migration dissolution models. For accurate predictions of stray gas dissolution, multiple dissolved gases must be considered. Multi-component analyses should extend to other stray gas investigations as well. Any gas-water mass transfer studies that may be conducted for other subsurface energy applications such as carbon sequestration or hydrogen storage should be considering multiple dissolved gas components. This may include a single component gas source, such as methane, interacting with background dissolved gases like nitrogen or oxygen, or could include a multi-component gas source such as hydrogen and cushion gas (methane, carbon dioxide, nitrogen) mixtures, or carbon dioxide impurities (carbon monoxide, sulfur dioxide, methane).

4.3 Contributions
This study contributed to understanding the role of background dissolved gases in a stray gas migration context. It demonstrated that background dissolved gases may be used as indicators of stray gas migration, potentially providing an additional tool to detect stray gas and to signify successful well repairs (Chapter 2). This research also contributed to the understanding of mass transfer in gas-water systems showing that a Sherwood correlation developed for a gas-water system is similar to the Sherwood models derived in the laboratory for NAPL models and that a constant mass transfer coefficient is sufficient for dissolution models (Chapter 3). Finally, this study highlighted the importance of including multiple dissolved gases in dissolution models to accurately describe methane gas retention times (Chapter 3). Contributions from this research will improve the monitoring tools available to identify and remediate stray gas in the field and advance the understanding of predicting aquifer recovery following a well repair, ultimately leading to improved environmental protection of shallow groundwater resources.
Appendix A

Experimental set up (Chapter 2)

Figure A.1: LTM set up including LED light panel, packed and saturated cell in a spill protection bin, camera, and blackout fabric covering the equipment when in use.

Figure A.2: Overview of experimental setup.
Figure A. 3: Total dissolved gas pressure probe attached to a weight to sink it to the bottom of the influent reservoir. A tygon tube connected to the total dissolved gas pressure (TDGP) probe was draped over the side of the influent reservoir and was connected to the influent pressure sensor (not shown) to keep it dry as reservoir emptied.

Figure A. 4: Flow-through cell showing the DO probe, TDGP probe, and inlet port (outflow from the flow cell) secured through a rubber stopper. Flow entered from the top of the flow-through cell and exits at the bottom outlet.
Figure A. 5: Close-up of flow-through cell and DO and TDGP probe connections. The flow-through cell was sealed by a rubber stopper through which the outlet TDGP sensor and probe were connected, a bleed valve was secured to vent any gas bubbles initially trapped in the cell, and a DO protective cap to allow for easy insertion of DO probe.
Appendix B

Raw initial saturated images (Chapter 2)

Images of the flow cell used to quantify gas saturations were captured using a Canon Rebel T6i (Canon EF-S 18-55mm lens). Camera settings were selected manually to obtain a high contrast between gas and water. Photos were captured using ISO3200, F16, and shutter speed of 1/30 for all experiments except for 3040F-1 that had a shutter speed of 1/20, making it appear brighter than the other photos.

Figure B. 1: Saturated backlit raw photos of the sand pack used for each 3040F experiments.

Figure B. 2: Saturated backlit raw photos of the sand pack used for each 3040S experiment.
Figure B. 3: Saturated backlit raw photos of the sand pack used for each 4060F experiment.

Figure B. 4: Saturated backlit raw photos of the sand pack used for each 4060S experiment.
Figure C. 1: Gas saturation maps at initial gas injection (gas breakthrough at surface), after prolonged gas injection, at relaxation (shortly after gas is shut off), and at the end of the post-repair dissolution for the 3040F experiments.
Figure C. 2: Gas saturation maps at initial gas injection (gas breakthrough at surface), after prolonged gas injection, at relaxation (shortly after gas is shut off), and at the end of the post-repair dissolution for the 3040S experiments.
Figure C. 3: Gas saturation maps at initial gas injection (gas breakthrough at surface), after prolonged gas injection, at relaxation (shortly after gas is shut off), and at the end of the post-repair dissolution for the 4060F experiments.
Figure C. 4: Gas saturation maps at initial gas injection (gas breakthrough at surface), after prolonged gas injection, at relaxation (shortly after gas is shut off), and at the end of the post-repair dissolution for the 4060S experiments.
Figure C. 5: Gas saturation maps for each experiment at the end of the active injection phase, immediately before gas flow was shut off, showing the unique gas migration pathways in similar sand packs.
Appendix D

Light transmission method calibration curves (Chapter 2)

Figure D. 1: Calibration curve for the 3040F-1 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw Ir/I$\alpha$ (blue) and the calibrated Ir/I$\alpha$ (orange) on a 1-to-1 line (black solid line).

Figure D. 2: Calibration curve for the 3040F-2 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw Ir/I$\alpha$ (blue) and the calibrated Ir/I$\alpha$ (orange) on a 1-to-1 line (black solid line).
Figure D. 3: Calibration curve for the 3040F-3 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw $Ir/Is$ (blue) and the calibrated $Ir/Is$ (orange) on a 1-to-1 line (black solid line).

Figure D. 4: Calibration curve for the 3040S-1 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw $Ir/Is$ (blue) and the calibrated $Ir/Is$ (orange) on a 1-to-1 line (black solid line).
Figure D. 5: Calibration curve for the 3040S-2 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw \textit{Ir/I}{\textsubscript{S}} (blue) and the calibrated \textit{Ir/I}{\textsubscript{S}} (orange) on a 1-to-1 line (black solid line).

Figure D. 6: Calibration curve for the 3040S-3 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw \textit{Ir/I}{\textsubscript{S}} (blue) and the calibrated \textit{Ir/I}{\textsubscript{S}} (orange) on a 1-to-1 line (black solid line).
Figure D. 7: Calibration curve for the 4060F-1 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw Ir/Is (blue) and the calibrated Ir/Is (orange) on a 1-to-1 line (black solid line).

Figure D. 8: Calibration curve for the 4060F-2 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw Ir/Is (blue) and the calibrated Ir/Is (orange) on a 1-to-1 line (black solid line).
Figure D. 9: Calibration curve for the 4060F-3 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw $Ir/Is$ (blue) and the calibrated $Ir/Is$ (orange) on a 1-to-1 line (black solid line).

Figure D. 10: Calibration curve for the 4060S-1 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw $Ir/Is$ (blue) and the calibrated $Ir/Is$ (orange) on a 1-to-1 line (black solid line).
Figure D. 11: Calibration curve for the 4060S-2 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw $Ir/Is$ (blue) and the calibrated $Ir/Is$ (orange) on a 1-to-1 line (black solid line).

Figure D. 12: Calibration curve for the 4060S-3 experiment comparing the measured gas volume to the gas volume calculated using Model C for the raw $Ir/Is$ (blue) and the calibrated $Ir/Is$ (orange) on a 1-to-1 line (black solid line).
Appendix E

Salt and dye tracer tests (Chapter 2 and 3)

Salt tracer tests were conducted in triplicate in 3040 (blue) and 4060 (orange) saturated sand packs to quantify dispersion. A 0.01 M NaCl solution was pumped through the system at 10.8 mL/min. Effluent samples were collected every 10 minutes for the first 30 minutes and every 1.5 min for the remainder of the test. The conductivity of each sample was measured immediately. Dye tracer tests were conducted in the 4060 saturated sand pack to verify dissolution of trapped gas was not influenced by preferential flow paths generated by the sand pack. Blue food colouring was mixed with DI water (10 drops per liter) and was pumped through the cell through the second and forth influent ports (with port 1 situated as the bottom most port). DI water was pumped through the remaining three influent ports.

![Graph](image)

**Figure E. 1**: Salt tracer tests performed in saturated 3040 (blue) and 4060 (orange) sand packs in triplicate.
Figure E. 2: Dye tracer test conducted in a saturated 4060 sand pack.
Appendix F

Dissolved oxygen stir test (Chapter 2)

A stir test was conducted for the DO probe to determine the response time in a mixed and non-mixed solution. A 125 mL flask of DI water was sparged with argon gas using a bubbling stone and a parafilm cover. The dissolved oxygen probe was then submerged into the flask immediately after removing the bubbling stone, measuring the DO concentration every 30 seconds. This test was performed with and without a stir bar and was necessary to show that the DO probe could respond fast enough without a stir bar to omit stirring from the experimental setup.

Figure F. 1: Response time of DO probe inserted into oxygen depleted water without stirring.
Figure F. 2: Response time of DO probe inserted into oxygen depleted water with stirring.
Appendix G

Steady-state and kinetic model inputs (Chapter 2 and 3)

Table G.1: Steady-state model input parameters by experiment for the Experiment Simulation set in Table 2.2.

<table>
<thead>
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<th>Test No.</th>
<th>$c_{wO_2}^i$ (mg/L)</th>
<th>$c_{wN_2}^i$ (mg/L)</th>
<th>$c_{wO_2}^j$ (mg/L)</th>
<th>$Q_w$ (mL/min)</th>
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<td>14.00</td>
<td>5.10</td>
<td>10.99</td>
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<td>10.81</td>
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<td>14.62</td>
<td>4.13</td>
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<td>8.87</td>
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<td>3.60</td>
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</table>
Table G. 2: Summary of kinetic model inputs for the single- and multi-component simulations. Cells that contain a list of four input values correspond to 3040F, 3040S, 4060F, and 4060S experiments, respectively.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Single-component</th>
<th>Multi-component</th>
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<tbody>
<tr>
<td>$c_{wO_2}$ (mg/L)</td>
<td>0</td>
<td>8.74&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>$c_{wN_2}$ (mg/L)</td>
<td>0</td>
<td>14.42</td>
</tr>
<tr>
<td>$c_{wAr}$ (mg/L)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$c_{wO_2}$ (mg/L)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td>5.59, 4.32, 4.07, 3.36</td>
</tr>
<tr>
<td>$c_{wN_2}$ (mg/L)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>9.19, 7.12, 6.65, 5.53</td>
</tr>
<tr>
<td>$c_{wAr}$ (mg/L)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>20.36, 28.44, 30.60, 34.91</td>
<td>20.44, 28.54, 30.35, 34.77</td>
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<tr>
<td>$c_{gO_2}$ (mg/L)</td>
<td>0</td>
<td>3.18, 1.03, 4.20, 1.20&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>$c_{gN_2}$ (mg/L)</td>
<td>0</td>
<td>5.28, 1.70, 6.99, 1.99&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>$c_{gAr}$ (mg/L)</td>
<td>1612.3</td>
<td>1600.9, 1608.7, 1597.18, 1608.05&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>$c_{wO_2}$ (mg/L)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0</td>
<td>0.102, 0.033, 0.134, 0.038</td>
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<tr>
<td>$c_{wN_2}$ (mg/L)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>0.084, 0.027, 0.112, 0.032</td>
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<tr>
<td>$c_{wAr}$ (mg/L)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>56.03, 56.30, 55.90, 56.28</td>
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<tr>
<td>$K_L$ ($\times 10^{-6}$ m$^3$/min)&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>6.2, 2.6, 0.11, 3.9</td>
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<tr>
<td>$Q_w$ (mL/min)&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>2.5, 10.4</td>
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<td>100000</td>
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<tr>
<td>$T$ (K)</td>
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<td>298</td>
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<tr>
<td>$H_{O_2}$ (-)</td>
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<tr>
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<tr>
<td>$H_{Ar}$ (-)</td>
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<td>$n$ (-)&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>0.33, 0.33, 0.31, 0.32</td>
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<tr>
<td>$\Delta t$ (min)</td>
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<td>1</td>
</tr>
<tr>
<td>$S_p$ (-)&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>0.019, 0.018, 0.073, 0.132</td>
</tr>
<tr>
<td>$V_T$ (ml)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1566.6</td>
<td>1566.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> measured

<sup>b</sup> calculated from steady-state model outputs
Appendix H

Mass transfer rate coefficient best fit curve (Chapter 3)

Using the solver tool in Excel, the Sherwood coefficients ($b'$, $c$ and $d$) were adjusted such that the difference of the sum of squares between the measured $K_L$ from the steady state model and the calculated $K^{sh}_L$ using the Sherwood expression approached zero. Figure H. 1 shows the 1-to-1 comparison between the predicted and measured $K_L$.

![Figure H. 1: Calibration curve for $K_L$ values measured in the steady-state model and $K^{sh}_L$ predicted using the Sherwood fit parameters developed for the gas-water system.](image)

Figure H. 1: Calibration curve for $K_L$ values measured in the steady-state model and $K^{sh}_L$ predicted using the Sherwood fit parameters developed for the gas-water system.
Appendix I
Supplemental kinetic model simulations (Chapter 3)

Upscaled mass transfer expressions in the NAPL literature by Christ et al. (2006), Falta et al. (2005), and Parker and Park (2004) generally use an expression that relates a concentration ratio to a mass ratio in place of saturation. Davidson, 2021 followed these upscaled mass transfer expressions for a series of laboratory scale gas injection experiments, arguing that gas saturation or gas volume was a false indicator of methane mass due to partitioning of background dissolved gases into the gas phase. Instead, mass of methane should be used, similar to the upscaled NAPL studies, in comparison with concentrations to better understand the mass transfer relationship. Based on these results, a third simulation was run in the kinetic dissolution model, using a transient $K_{L}^{sh}$ updated at each time step as a function of mass (black dashed). The results in Figure I.1 did not indicate an improved fit from the transient $K_{L}^{sh}$ by saturation (green dashed).
Figure I. 1: Kinetic model simulations predicting gas saturations and DO concentrations during dissolution using a constant $K_L$ (orange solid line), a transient $K_{L,sh}^S$ as a function of saturation (green dashed line), and a transient $K_{L,sh}^M$ as a function of mass (black dashed line) for the 3040F (a, b), 3040S (c, d), 4060F (e, f) and 4060S (g, h) experiments (open circles).
References


