INVESTIGATING GAS PHASE PROCESSES IN GROUNDWATER

INVESTIGATING GAS PHASE PROCESSES IN NATURAL AND HYDROCARBON-CONTAMINATED GROUNDWATER

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ABSTRACT

Here the nature of gas phase processes and their implications for flow and transport were examined using a pilot-scale, 2-dimensional, laboratory tank instrumented for direct, *in situ* trapped gas measurements. Experimental conditions mimicked an unconfined, homogeneous sand aquifer with horizontal flow. Key areas of investigation included i) trapped gas dissolution following a water table fluctuation; and ii) gas phase dynamics within a hydrocarbon plume experiencing dissolved gas production via biodegradation.

In the first experiment, dissolution occurred as a diffuse, wedge-shaped front propagating down-gradient in the tank over time, with enhanced dissolution at depth. Front advancement at the deepest monitoring point was 4.1 - 5.7x faster. This dynamic, depth-dependent pattern was mainly attributed to increased dissolved gas solubility. An estimated 12% increase in quasi-saturated hydraulic conductivity (K_{qs}) also contributed to greater dissolution at depth. Overall, the dissolution front near the water table advanced 1 m down-gradient in 344 days, suggesting that gas trapped shallowly will likely persist for significant periods of time. The utility of total dissolved gas and monitor its dissolution were also demonstrated.

During the second experiment, biodegradation occurred under variable redox conditions, ranging from denitrification to methanogenesis. Significant *in situ* increases in trapped gas were observed within the tank over 330 days. Maximum gas saturations never exceeded 27% of pore volume even during

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continued dissolved gas production, indicating ebullition upon reaching a gas phase mobilization threshold. Consequently, associated reductions in K_{qs} were restricted to a factor of 2 or less, but still appeared to alter the groundwater flow field. While trapped gas increases within the biodegradation plume were expected, declines in gas saturations were also observed. Thus, the overall pattern of trapped gas growth exhibited high spatial and temporal variability. Influencing factors included changes in hydrocarbon inputs and microbial controls on redox zonation, in addition to ebullition and changes in groundwater flow; emphasizing that gas phase growth in contaminant plumes will be highly complex and dynamic in the natural systems.

Given the impacts on hydraulic conductivity, and the fate and transport of volatile compounds, an improved understanding of quasi-saturated conditions will be beneficial for various groundwater applications, from recharge and paleoclimate studies to site characterizations and remediation strategies.

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LIST OF ALL ABBERVIATIONS & SYBMOLS

Symbol	Name
d_{50}	Mean grain size
d ₆₀ /d ₁₀	Coefficient of uniformity
1-D	One dimensional
2-D	Two dimensional
BEC	Bulk electrical conductivity
CCIW	Canada Centre for Inland Waters
C_{gi}	Dissolved concentration of gas <i>i</i>
DIC	Dissolved inorganic carbon
DO	Dissolved oxygen
g	Acceleration due to gravity
GC	Gas chromatography
GW	Groundwater
GWS	In situ groundwater sampler
h	Depth below water table
HDPE	High-density polyethylene plastic
HID	Helium ionization detector
НТ	Head tank
IC	Ion exchange chromatography
ICP-OES	Inductively coupled plasma - optical emission spectrometry
IW	Injection well
K	Hydraulic conductivity
K _{Hi}	Henry's Law constant for gas species <i>i</i>
K _{qs}	Quasi-saturated hydraulic conductivity
Kr	Relative hydraulic conductivity
Ks	Saturated hydraulic conductivity
MW	Monitoring well

n Overall bulk porosity

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- *ne* Maximum effective porosity
- NAPL Non-aqueous phase liquid
 - σ Surface tension of water
 - *ρ* Density of water
 - *ρ_b* Bulk density
 - *p*_s Particle density
- **P**atm Barometric pressure
- *P_c* Capillary pressure
- **p**_{gi} Partial pressure of gas species *i*
- **P**_G Total trapped gas pressure
- *P*^{*}_{*G*} Calculated bubbling pressure
- PGS Passive gas sampler
- PLFA Phospholipid fatty acid
- **P**_{TDG} Total dissolved gas pressure
- **P&T GS-MS** Purge and trap, gas chromatography mass spectrometry
 - **PV** Cumulative pore volume passed
 - **PVC** Polyvinyl chloride
 - **P**_w Water pressure
 - *q* Volumetric flux of groundwater
 - **Q** Total discharge rate out of lane
 - *r*₁ & *r*₂ Radii of curvature of trapped gas ganglia
 - **R** Universal gas constant
 - **R2** Shaping parameter for graphing methods used in Surfer Software
 - **R**² Coefficient of determination
 - **RSD** Relative standard deviation
 - *S* Salinity
 - **S**_{CG} Critical gas saturation
 - **S**_G Gas saturation

STDEV	Standard deviation
t	Time
Т	Absolute temperature
TCD	Thermal conductivity detector
TDR	Time Domain Reflectometry
UV/Vis-S	UV/Visible spectrum spectrometry

 $\overline{\mathbf{v}}$ Average linear pore water velocity

PREFACE

This thesis contains five chapters in total. Chapter 1 represents a brief overview of the current scientific literature on gas phase dynamics in groundwater systems; in addition to outlining the key research objectives of this dissertation. Chapter 2 provides an in depth description of the experimental design and materials used, including the porous medium. The results of this thesis were split into two separate chapters to reflect the opposing nature of the experiments conducted, where trapped gas was fated to disappear (Chapter 3), or to form, expand and undergo transport (Chapter 4). Note in Chapter 3, trapped gas was commonly described as 'entrapped air', which specifically refers to a residual gas phase trapped because of water table fluctuations. Furthermore, Chapter 3 contains co-authored material accepted for publication. The result chapters are presented as:

- **Chapter 3:** McLeod, H.C., J.W. Roy, and J.E. Smith. 2015. Patterns of entrapped air dissolution in a two-dimensional pilot-scale synthetic aquifer. *Ground Water*, 53 (2), 271-281.
- **Chapter 4:** A pilot-scale laboratory investigation of gas phase dynamics within a groundwater hydrocarbon plume.

In the final chapter, the key contributions of this thesis are summarized with recommendations for future research.

The dissertation author (H.C. McLeod) designed and maintained the indoor aquifer laboratory at the Canada Centre of Inland Waters (CCIW); in addition to conducting all experiments presented in this thesis, in close

consultation with Dr. J.W. Roy. However, K. Evelegh characterized the relative hydraulic conductivity – trapped gas saturation relation from Chapter 2 with technical assistance from H.C. McLeod. Analytical quantification of major cation (ICP-OES), hydrocarbon (P&T GC-MS) and dissolved gas (GC) concentrations for Chapter 4 were carried out by H.C. McLeod; whereas major nutrient (S) and anion (IC) concentrations were processed by Pam Collins. Analysis and interpretation of all experimental data was completed by H.C. McLeod under the supervision of Dr. J.W. Roy and Dr. J.E. Smith (co-authors); who also as provided expertise guidance on the presentation and discussion of the experimental results, in addition to detailed editorial comments during manuscript preparation.

CHAPTER 1

An Overview of Gas Phase Dynamics in Groundwater

1.1 Introduction

Natural and contaminated groundwater inherently contain dissolved gases as a result of atmospheric exposure prior to infiltration and recharge, biogeochemical reactions occurring both above and below the water table (Freeze and Cherry 1979); in addition to anthropogenic intervention, such as remediation techniques. Typically, the most abundant dissolved gases are nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂), hydrogen sulfide (H₂S) and methane (CH₄). Other species of interest may include hydrogen (H₂) and the noble gases; however these exist in groundwater at trace amounts. In general, dissolved gases are an important aspect of the subsurface environment with significant implications for a wide range of groundwater issues.

For instance, noble gases can be used as environmental tracers, providing information on physical groundwater processes, such as sources and ages (e.g. Busenberg and Plummer 1992; 2000), as well as paleoclimates (e.g. Mazor 1972; Stute et al. 1992). At contaminated sites, dissolved oxygen is a favoured electron acceptor for *in situ* bioremediation efforts since it has one of the highest redox potentials and commonly results in rapid degradation rates (refer to Wilson and Bouwer 1997; Wiedemeier et al. 1999). In addition, the metabolic products of biodegradation, such as CO₂, H₂S, CH₄ and H₂, have been used to identify and evaluate the predominant redox reactions occurring in groundwater systems during site characterizations and/or remediation schemes (Lovley et al. 1994; Chapelle et al. 1995; Wiedemeier et al. 1999). Biodegradation products can also cause major resource management issues.

For example, H_2S concentrations greater than 1.5 μ M (0.05 mg/L) renders water non-potable due to its offensive odor (Health Canada 2003); whereas, CH₄ gas accumulation in drinking water wells and/or buildings can present significant explosion hazards (e.g. Osborn et al. 2011; Ma et al. 2014). Thus, the measurement of dissolved gas concentrations has become widespread in groundwater and contaminant hydrology.

However, previous research has also shown that the presence of trapped gas 'bubbles', representing a separate immiscible phase in groundwater systems, can alter the distribution and concentration of dissolved gases and other volatile compounds (e.g. non-aqueous phase liquid (NAPL) contaminants) through significant mass transfer effects and/or hydraulic conductivity changes, affecting flow and transport processes. Therefore, in many cases, monitoring dissolved gases within the groundwater zone is intrinsically linked to understanding the fate of trapped gas; which may involve its dissolution into the aqueous phase; or in contrast, its expansion and growth with the potential for gas mobilization (ebullition). These gas phase dynamics and their associated impacts in shallow groundwater systems are the primary focus of this dissertation.

1.2 Trapped Gases in Groundwater Systems

A trapped gas phase is isolated from the atmosphere within otherwise water-saturated porous or fractured media below the top of the capillary fringe, thereby producing regions of quasi-saturation within the groundwater zone (Faybishenko 1995). Different configurations of trapped gas, ranging from small,

pore-size bubbles, in both dead-end and open pores, to ganglia possessing multiple branches spanning several pores, can exist and are spatially fixed by capillary forces (Roy and Smith 2007). Significant but variable trapped gas saturations up to 54% of the pore volume have been reported for groundwater systems (refer to Fry et al. 1997; Marinas et al. 2013; and references therein).

It has been well known for the past 70 years that atmospheric air and soil gas can be trapped as a residual gas phase during water table fluctuations (also referred to as 'entrapped air' in Chapter 3) (Smith and Browning 1942; Christiansen 1944). Water table oscillations can occur naturally, as a result of evapotranspiration, infiltration, recharge and groundwater-surface water interactions, or they can be caused by groundwater resource exploitation. Numerous studies have demonstrated that the degree of residual gas saturation varies with the soil type and grain size distribution (Constantz et al. 1988), the rate of infiltration and initial soil moisture content (Fayer and Hillel 1986a, 1986b), and pore structure or geometry (Peck 1969; Wardlaw 1982). It also can be enhanced by the presence of heterogeneity (Silliman et al. 2002; Dunn and Silliman 2003). Moreover, a gas phase can be introduced to the groundwater zone following the injection of gases, such as during air rotary drilling (Driscoll 1986; Manning et al. 2003), or during remediation activities (e.g. air sparging, Fry et al. 1997; Roosevelt and Corapcioglu 1998; Balcke et al. 2007, 2011). Note that the active vertical advection of gas through continuous channels during injection is not considered here to be trapped gas, though subsequent mobility of trapped gases is considered below in Section 1.3.

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Trapped gas may also form autogenously when dissolved gases in groundwater achieve supersaturation. Dissolved gas supersaturation can be attained through physicochemical decreases in gas solubility, such as an increase in temperature (e.g. during thermal remediation technologies, Krol et al. 2011) and/or a decrease in pressure (e.g. during upward groundwater flow in discharge zones, Klump et al. 2008; or during groundwater extraction, Tsimpanogiannis and Yortsos 2002). Supersaturation can also be achieved where dissolved gases are being produced by biogeochemical processes, such as in wetlands (e.g. Baird et al. 2004; Strack et al. 2005) or at sites with agricultural (e.g. Blicher-Mathiesen et al. 1998) and/or industrial (e.g. Amos et al. 2005) contamination. In fact, the biogeochemical reactions that have the greatest capacities to potentially induce trapped gas formation include denitrification and methanogenesis, given the low aqueous solubilities of N₂ and CH₄ gas (Ryan et al. 2000; Amos et al. 2005). Furthermore, groundwater remediation schemes that inject gas-supersaturated waters (Fry et al. 1997; Enouy et al. 2011) or that promote inorganic chemical reactions having gaseous products, such as chemical oxidation treatments (e.g. Schroth et al. 2001) and/or permeable reactive barriers (Zhang and Gillham 2005; Kamolpornwijit et al. 2003; Kamolpornwijit and Liang 2006; Williams et al. 2007) can result in autogenous gas phase formation (i.e., exsolution), as well.

Several studies have shown that *in situ* trapped gas formation will not occur until the magnitude of the dissolved gas supersaturation (or build-up of total dissolved gas pressure) exceeds some critical bubbling pressure, which is

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considered as the sum of the prevailing water pressure, capillary pressure and potentially in some circumstances, a nucleation energy barrier (Li and Yortsos 1994; 1995; Tsimpanogiannis and Yortsos 2002). However, nucleation barriers do not apply where meta-stable gas cavities or seed bubbles pre-exist, which is believed the general case for most freshwater aquifers (Jones et al. 1999a; 1999b; Or and Tuller 2003). Indeed, it is common to observe autogenic gas phase formation even at relatively low dissolved gas supersaturations (Jones et al. 1999a). Overall, it is likely that the occurrence of a trapped gas phase in shallow groundwater systems may be ubiquitous due to resource development and contamination, remediation strategies, and natural processes causing water table fluctuations and/or exsolution.

1.3 Fate of Trapped Gases

Following gas phase entrapment and/or formation, mass will be exchanged across the gas-water interface in order to establish equilibrium between the dissolved gases in the groundwater and those in the trapped gas phase. Numerous studies (e.g. Cirpka and Kitanidis 2001; Holocher et al. 2003; Geistlinger et al. 2005; Amos and Mayer 2006a; Balcke et al. 2007; Mumford et al. 2010) have shown that this inter-phase mass transfer can result in the dissolution or expansion of the gas phase, depending on the total trapped gas pressure, which is a function of the prevailing water pressure (also accounts for changes in barometric pressure) and the capillary pressure related to the interfacial tension of the curved gas-water interface; in addition to the dissolved gas concentrations, potentially influenced by biogeochemical reactions and remediation techniques, as previously mentioned in Section 1.2; compound-specific partitioning coefficients, that is, the aqueous solubilities of different gases, dependent on groundwater temperature and salinity; and finally, the different aqueous diffusivities of the relevant gas species when kinetic effects of inter-phase mass transfer are considered. Therefore, multi-component gas-water partitioning is highly complex and dynamic, often occurring in opposite directions as equilibrium is established for each individual gas compound (Cirpka and Kitanidis 2001; Balcke et al. 2007; Oswald et al. 2008). Note, more detailed descriptions of gas-water partitioning and pertinent theory on gas phase dynamics, including governing equations, is provided in subsequent Chapters of this dissertation.

In general however, a gas phase will dissipate into the aqueous phase over time when the passing groundwater is under-saturated with dissolved gases compared to the local trapped gas pressure. This dissolution condition is true for recharged groundwater originally in equilibrium with the atmosphere that comes into contact with trapped gas derived from water table fluctuations (Williams and Oostrom 2000; Holocher et al. 2002; 2003; Klump et al. 2008; Haberer et al. 2012); in addition to residuals after gas injection during remediation activities (Fry et al. 1997; Geistlinger et al. 2005; Balcke et al. 2007; 2011). Mass transfer occurs since the trapped gas is under higher total gas pressure, with the dissolution potential increasing at deeper depths below the water table, that is, at greater prevailing water pressures, as previously discussed by Holocher et al.

(2003) and Klump et al. (2008). Dissolution also may occur or be enhanced where gases are consumed by biogeochemical reactions, such as aerobic respiration (Ryan et al. 2000; Amos et al. 2005).

Alternatively, increases in trapped gas saturations (i.e., gas phase expansion likely coupled with in situ formation, recall Section 1.2) have been inferred from a variety of indirect measurements at several field settings due to biogenic gas production, supersaturating the groundwater with dissolved gases. For example, these settings have included: deep organic-rich groundwater (Fortuin and Willemsen 2005), under landfills (Solomon et al. 1992; van Breukelen et al. 2003; Purtschert et al. 2004) and petroleum fuel spills (Baedecker et al. 1993; Revesz et al. 1995; Amos et al. 2005), and in permeable reactive barriers (Williams et al. 2007) as a result of CH₄ generation; or agricultural areas with high nitrate loadings (Blicher-Mathiesen et al. 1998; Visser et al. 2007; 2009) as a consequence of N_2 production. These field observations are also corroborated by numerical modeling efforts (e.g. Amos and Mayer 2006a). though largely empirically-based; and small-scale, laboratory experiments investigating gas phase processes during denitrification (lstok et al. 2007) and methanogenesis (Amos and Mayer 2006b). Other laboratory studies have also shown that the presence of volatile non-aqueous phase liquid (NAPL) compounds contribute additionally to the total dissolved gas pressure and as a result can induce spontaneous gas phase growth through multi-component partitioning, as well (Roy and Smith 2007; Mumford et al. 2008; 2009a; 2009b). In this case, gas phase expansion may also be cumulatively influenced by

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capillary pressure changes via interfacial tension reductions due to NAPL contamination (Roy and Smith 2007); however, NAPL-induced capillary pressure changes are not pertinent to this dissertation.

Furthermore, continued expansion can result in the fragmentation and subsequent vertical mobilization of a gas phase, as buoyancy forces surpass the local capillary forces, which trap the gas ganglia in situ (Tsimpanogiannis and Yortsos 2004; Roy and Smith 2007). Laboratory observations of gas phase advection (ebullition) in coarse-grained porous media have described it as chaotic, incoherent macro-cluster gas flow that is punctuated by brief, intermitted vertical transport events that follow a tortuous path of minimal capillary pressure requirements (Geistlinger et al. 2006; Istok et al. 2007; Mumford et al. 2009a; 2009b). Trapped gas mobilization occurs predominantly upwards due to the density differences between the phases and is only sustained through continued mass transfer and/or the coalescence of multiple gas clusters (Fry et al. 1997; Geistlinger et al. 2006; Mumford et al. 2009a; 2009b). In real aquifer systems however, heterogeneity can hinder vertical gas phase advection, resulting in substantial gas accumulation (i.e., trapped gas pools) on the underside of capillary layers (e.g. Glass et al. 2000) prior to ebullition. Indeed, sudden, high volume, ebullitive gas release associated with substantial gas accumulation have been noted in saturated bogs, peatlands (e.g. Rosenberry et al. 2006) and at several denatured ethanol-impacted groundwater sites (e.g. Sihota et al. 2013).

1.4 Importance of Trapped Gases

Conditions of quasi-saturation can have significant implications for groundwater flow and subsequent repercussions on the fate and transport of volatile contaminants and dissolved gases. For instance, the presence of trapped gas can effectively reduce the saturated hydraulic conductivity by a factor of 2 -20 (e.g. Faybishenko 1995; Fry et al. 1997; Sakaguchi et al. 2005; Marinas et al. 2013). Such reductions can limit groundwater flow and ultimately, decrease infiltration and groundwater recharge (Christiansen 1944; Constanz et al. 1988; Heilweil et al. 2004), in addition to saltwater intrusion (Dror et al. 2004) and operational efficiencies of remediation techniques (e.g. chemical oxidation treatments, Schroth et al. 2001; and permeable reactive barriers, Zhang and Gillham 2005); and/or create stagnant flow zones (Ronen et al. 1989; Ryan et al. 2000). This in turn, can influence the transport of solutes and microbes within the groundwater zone (Orlob and Radhakrishna 1958; Berkowitz et al. 2004). In addition, trapped gas-induced variations to the hydraulic conductivity field may also cause deflections in groundwater flow around contaminant source zones (Amos and Mayer 2006a) and/or permeable reactive barriers (Fryar and Schwartz 1998), affecting microbial biodegradation rates and remediation efforts.

Interactions with trapped gas can also affect groundwater biogeochemistry via mass transfer. Dissolution of entrapped atmospheric air can result in a supersaturation of dissolved gases relative to atmospheric equilibrium, which is a widespread groundwater phenomenon known as 'excess air' (Heaton and Vogel 1981). This 'excess air' can affect the interpretation of dissolved gases commonly

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used as environmental tracers, such as sulfur hexafluoride (Busenberg and Plummer 2000) and tritium-helium (Schlosser et al. 1988) in groundwater dating techniques. It also has implications for paleoclimate studies using noble gas infiltration or recharge temperatures (e.g. Wilson and McNeill 1997; Aeschbach-Hertig et al. 2000). Finally, 'excess air' can represent a significant source of dissolved oxygen that otherwise would not be available for contaminant bioremediation (Williams and Oostrom 2000; Holocher et al. 2003; Haberer et al. 2012). Moreover, mass transfer effects can influence the transport dynamics of dissolved gases and other volatile compounds in groundwater, including the retardation of partitioning tracers and volatile contaminants, such as chlorofluorocarbons, helium and sulfur hexafluoride (Gupta et al. 1994; Cirpka and Kitanidis 2001; Clark et al. 2005); or the replenishment of oxidants (e.g. dissolved oxygen, Fry et al. 1995; 1996). These effects can impact site characterizations and remedial design applications (Donaldson et al. 1998).

Furthermore, vertical mobilization of the gas phase can affect contaminant vapour (e.g. NAPL compounds) and/or biogenic gas (e.g. N₂, CO₂, H₂S, CH₄) transport, potentially exposing formerly unaffected regions of the subsurface to contamination (Amos and Mayer 2006b, Roy and Smith 2007; Mumford et al. 2010); in addition to posing significant explosion and asphyxiation risks due to gas accumulation in wells, soils and/or buildings (Spalding et al. 2011; Sihota et al. 2013; Ma et al. 2014). The upward flux of biogenic gases via ebullition from wetlands and aquifers are typically large in comparison to diffusive fluxes and as a result, may contribute significantly to global greenhouse gas emissions

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(Rosenberry et al. 2003; 2006; Amos and Mayer 2006b). Lastly, gas phase expansion and movement in the presence of a non-aqueous phase liquid (NAPL) can mobilize the NAPL (Roy and Smith 2007; Mumford et al. 2009a), thus affect contaminant mass transfer in NAPL source zones, potentially leading to greater groundwater contamination.

1.5 Research Objectives

In summary, the presence of a trapped gas phase is expected to create highly complex multiphase systems, in both natural and contaminated aquifers, with temporally- and spatially- variable gas-water interactions, biogeochemical conditions, hydraulic properties and transport processes. Currently however, gas phase dynamics in aguifers, especially contaminant plumes, are not fully understood since previous research has largely been limited to small-scale, onedimensional column experiments and/or peripheral observations at field sites. Therefore, this dissertation adopted an innovative experimental approach to better examine the *in situ* nature of trapped gas processes in natural porous media at a field-representative scale. This was done using direct, nearcontinuous trapped gas measurements with dissolved gas and aqueous geochemical analyses in a highly-instrumented, pilot-scale, laboratory tank (240 cm wide × 600 cm long × 180 cm deep). Experimental conditions mimicked a homogeneous, unconfined sand aguifer with horizontal groundwater flow and a residual gas phase following a water table fluctuation. In total, two tank
experiments were conducted over a 716 day period and the key research objectives included:

- 1) Characterizing the 2-dimensional pattern of trapped gas dissolution within the zone of fluctuating water table (Figure 1.2A) since previous dissolution studies have largely focused on the formation and fractionation of 'excess air' using a variety of gas-water exchange models (e.g. Kipfer et al. 2002; Aeschbach-Hertig et al. 2008); with experimental work mainly restricted to small-scale (\leq 100 cm), onedimensional systems (e.g. Holocher et al. 2003; Geistlinger et al. 2005; Klump et al. 2008). It was anticipated that depth-dependent effects on mass transfer from the trapped gas and on quasi-saturated hydraulic conductivity would lead to a temporally- and spatially- variable dissolution pattern. A secondary objective of this experiment was to test the effectiveness of total dissolved gas pressure (P_{TDG}) probes for monitoring the fate of a lingering gas phase, as originally proposed by Manning et al. (2003). (Chapter 3)
- 2) Investigating spatial and temporal changes in a gas phase within a hydrocarbon plume experiencing dissolved gas production via biodegradation (Figure 1.2B). Of particular interest was the pattern of biogenic gas production and resultant trapped gas dynamics, including the potential for gas phase mobilization; which were expected to be highly complex, varying significantly with the evolving biogeochemical conditions and microbial community; in addition to contaminant

distribution, groundwater flow and pressure patterns. To date, biogenically-driven gas phase dynamics at hydrocarbon-impacted field sites have only been inferred (e.g. Baedecker et al. 1993; Revesz et al. 1995; Amos et al. 2005; Sihota et al. 2013) and supporting laboratory work has been restricted to small-scale systems (\leq 100 cm) with stagnant (no flow) conditions (Amos and Mayer 2006b; Istok et al. 2007). **(Chapter 4)**



Figure 1.1: A conceptual model of the trapped gas processes examined in this dissertation including its dissipation into the aqueous phase following entrapment during a water table fluctuation (A); and its growth and subsequent vertical mobilization due to biogenic gas production within a degrading dissolved hydrocarbon plume (B4). The dissolved hydrocarbon plume (4) represented here, is emanating from a light non-aqueous phase liquid (*LNAPL*) source zone containing both residual (2) and free-phase (i.e., *LNAPL* pool, 3) contamination as a result of a leaky underground storage tank (1). Note this model (modified from Marinas et al. 2013) is not to scale.

Overall, it is anticipated that the results of this dissertation will provide new

insights into the multidimensional nature of trapped gas dynamics and their

implications for groundwater flow, the fate and transport of volatile contaminants and dissolved gases; ultimately, emphasizing the relevance of gas phase processes in shallow groundwater systems. An improved understanding of quasisaturated conditions will likely be beneficial for a wide variety of groundwater applications, from recharge and paleoclimate studies to site characterizations, management and remediation strategies.

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CHAPTER 2

Methods and Materials

2.1 Introduction

In total, two experiments were conducted from June 2011 to September 2013. Specific methodology sections are included in each data chapter (Chapters 3 and 4). However, the purpose of the current chapter is to provide a more detailed description of the selected porous medium, tank construction and the synthetic groundwater; as well as the instrumentation, laboratory methods and analytical procedures used, for reference.

2.2 Porous Medium

Unground BARCO silica sand supplied by Opta Minerals (Waterdown, Ontario, Canada) was used because it offers high chemical purity with very low metal oxides and organic carbon content (Table 2.1). It is also available in large quantities at a relatively low cost. All sand was pre-washed with water, dried and screened by Opta Minerals to a medium grade designated as M49. The calculated mean grain size (d_{50}) is approximately 0.30 mm. In addition, the sand is highly uniform in nature, as indicated by its narrow particle size distribution (not shown) and high coefficient of uniformity (d_{60}/d_{10}) (Table 2.1). Pertinent hydraulic properties of the BARCO M49 sand were characterized at a desired bulk density of 1.65 g/cm³. For instance, the saturated hydraulic conductivity (K_s) was determined using small-scale constant head permeameters, which were first flushed with carbon dioxide followed by de-aired water. This CO₂-H₂O pretreatment is a widely accepted practice to attain complete water saturation in soil columns (Faybishenko 1995; Zlotnik et al. 2007). Measured K_s exhibited good

reproducibility, as indicated by the small standard deviation (Table 2.1), and were consistent with reported values for uniform sands (Bear 1972; Marinas et al. 2013).

Physical Properties				
Mineral ¹	Silicon Dioxide, Quartz			
Colour ¹	White			
Grain Shape ¹	Round to Sub-round			
Hardness ¹	7 Mohs			
Particle Density ¹	2.65 g/cm			
Solubility ¹	Insoluble			
Mean Grain Size	0.30 mm			
Coefficient of Uniformity (d_{60}/d_{10})	1.72			
Chemical Composition ¹				
Total Crystalline Silica (SiO ₂)	99.70%			
Aluminum Oxide (Al ₂ O ₃)	0.14%			
Iron Oxide (Fe ₂ O ₃)	0.02%			
Potassium Oxide (K ₂ O)	0.04%			
Sodium Dioxide (Na ₂ O)	< 0.01%			
agnesium Oxide (MgO) < 0.01%				
Calcium Oxide (CaO)	< 0.01%			
Hydraulic Properties				
Average Bulk Density \pm 2STDEV ^{2, 3, 4}	1.65 ± 0.03 g/cm ³			
Porosity	37.6%			
Air Entry Pressure ⁴	-26 cmH ₂ O			
Sat. Hydraulic Conductivity ± 2STDEV 2,	³ 0.045 ± 0.01 cm/s			

Table 2.1: All relevant physical, chemical and hydraulic properties of BARCO M49 Sand.

¹ Reproduced from Opta Minerals.
 ² Constant head permeameter results.
 ³ BARCO M49 1-D column experiments after Marinas et al. (2013).
 ⁴ Derived from main drainage curves measured in volumetric pressure plate extractors.

The main moisture characteristic curves for the M49 sand were measured in a Volumetric Pressure Plate Extractor. *In situ* volumetric moisture contents and soil water pressures were captured using a Time Domain Reflectometry (*TDR*) probe and a pressure transducer equipped with a tensiometer, respectively. The sand cores were slowly saturated and then drained to residual saturation using a constant head technique. Measured water retention curves (not shown) featured a well-defined air entry pressure (Table 2.1), indicating the expected height of the capillary fringe in homogeneous M49 sand packs, as well as the capillary pressure required for the expansion-migration of trapped gas ganglia into neighboring pore spaces. Furthermore, the observed saturated volumetric moisture contents varied from 28.0% to 35.2% between duplicate wetting and drying cycles, suggesting residual trapped gas contents could range up to 7.2% of the bulk volume following a water table fluctuation.

Finally, the quasi-saturated hydraulic conductivity (K_{qs}) as a function of trapped gas saturation (S_G) in BARCO M49 sand packs was measured in small-scale, 1-D laboratory column experiments according to the methods described by Marinas et al. (2013). These hydraulic conductivity tests for both saturated and quasi-saturated conditions were performed using a constant head technique and *TDR* probes, which directly monitored trapped gas contents as the position of the water table was increased, in a stepwise fashion, up to 180 cmH₂O. The two BARCO M49 column experiments, which had differing amounts of initial trapped gas (i.e., 11.1% vs. 5.6% for Trial A & B), were plotted with relative hydraulic conductivity – gas saturation results for similar sands (i.e., Ottawa and M56) from

Marinas et al. (2013) (Figure 2.1). The linear regression result of the combined dataset presented in Figure 2.1 can be used to relate changes in quasi-saturated hydraulic conductivity and thus, groundwater flow to differences in trapped gas contents.



Figure 2.1: Relevant relative hydraulic conductivity ($K_r = K_{qs}/K_s$) data as a function of trapped gas saturation (S_G) from Marinas et al. (2013) (i.e., Ottawa sand (green) and M56 sand (blue)) was superimposed with BARCO M49 sand data (black) from similar 1-D column experiments. The line represents the combined linear regression result which was forced through (0, 1).

Ultimately, the selection of an appropriate porous medium and its subsequent characterization was an important initial step in this dissertation to ensure good analytical control while still representing the natural environment. Also, knowledge of the sand properties can facilitate data interpretation.

2.3 Experimental Set-Up of the Tank

The pilot-scale synthetic aquifer was assembled using approximately 36.5 metric tonnes of BARCO M49 sand in a 304 L stainless steel tank (600 cm long × 240 cm wide × 180 cm deep) located indoors at the Canada Centre for Inland Waters (CCIW) in Burlington, Ontario, Canada. The tank was divided lengthwise into three separate test lanes, each 80 cm wide with an open reservoir or head tank (*HT*, 80 cm wide × 75 cm long) located at one end (Figure 2.3). The *HTs* were separated from the aquifer (i.e., the sand-packed section) by a steel perforated plate affixed with a non-woven polypropylene geotextile (Nilex, Toronto, Ontario, Canada). Each lane was fitted with *in situ* monitoring and sampling equipment during the packing procedure (January 2010 to April 2010); however, only the two outside lanes (Lanes 1 and 3) were used in the experiments (Figure 2.3A).

These lanes were manually packed (Figure 2.2) in 5 cm lifts (0.40 metric tonnes of sand per layer) to achieve a fully reproducible homogeneous porous medium and allow fundamental gas phase behaviours to be investigated without added complexities. Before packing, all sand was wetted to a gravimetric water content of 4.0% using an industrial cement mixer to avoid particle size segregation. Each lift was then poured into the desired lane over five trips, leveled by hand and packed down using 25×25 cm² flat iron tampers. To ensure consistency between different packers, the tampers were raised 10 cm from surface and then released four to five times over the same section of sand before moving on. Once packed down, the surface was disturbed with a rake before

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adding the next layer to minimize horizontal layering effects between individual lifts (Figure 2.2).



Figure 2.2: Pictorial summary of the packing procedure: A) delivery of 57 metric tonnes of BARCO M49 sand in 50 lb bags; B) adding 4.0% gravimetric moisture content to sand with industrial cement mixer; C) dumping 0.40 metric tonnes into each lane per 5 cm lift; D) distributing sand evenly throughout lane; E) packing down a 5 cm lift with 25 × 25 cm² iron tampers; F) disturbing surface of lift with rake before next layer was added.

The mass of dry sand added (and spilled) during packing was recorded for calculation of the overall bulk density (ρ_b), given the measured volume of the filled tank. The overall bulk porosity (*n*) of the packed tank was 37.6% based on the calculated bulk density (ρ_b) and a particle density (ρ_s) of 2.65 g/cm³ (Table 2.1). Following a year of intermitted use, Lanes 1 and 3 were drained and then inoculated with a site microbial community in September 2011 to help ensure the aquifer would have a viable population of micro-organisms. Approximately 1.5 kg

of site sample previously exposed to hydrocarbon contamination was added to 200 L of deionized water and vigorously mixed to promote microbially desorption from the sediment grains (e.g. Jewett et al. 1995; Li and Logan 1999). The microbially-spiked water was then rained over the sand surface of a single lane with a custom sprinkler system while its head tank was simultaneously backfilled with synthetic groundwater at approximately the same rate. In total, this process was repeated fifteen times for each lane in order to fully saturate the aquifer over a two day period. Thus, inoculation also mimicked a 155 cm rise in the water table during recharge, entrapping atmospheric air and creating conditions of quasi-saturation. After inoculation and initial gas entrapment, the tank was sealed with a heavy-duty polyethylene plastic and hooked up to a custom exhaust system as an indoor air precaution. A large opaque plastic tarp was then loosely place over top to minimize ultraviolet light exposure and growth of algae on the sand surface.

Synthetic groundwater (discussed later) was then gravity fed from two 1400 L HDPE source water reservoirs into the head tanks, which were equipped with industrial brass float valves to maintain the up-gradient constant head boundary conditions (Figure 2.2). Groundwater flow was generated by pumping with a peristaltic pump from one fully screened 4-inch PVC withdrawal well centered at the end of each lane, 520 cm from the *HTs*. Refer to Chapters 3 and 4 for the specific withdrawal well rates (i.e., the flow velocities) applied during each experiment. Note that a pore volume passed (*PV*) was calculated as the water volume within the sand-filled section of a single lane (1 PV = 2760 L).



Figure 2.3: Bird's eye view of the pilot-scale tank showing each test lane (A) and a panoramic view of the overall laboratory experimental set-up at the Canada Centre for Inland Waters, Burlington, Ontario, Canada (B).

All effluent was collected in an alternate 1400 L HDPE reservoir to undergo chlorination before being gravity fed through two prefabricated, 208 L liquid phase activated carbon vessels (Maple Leaf Environmental Equipment, Brockville, Ontario, Canada) (Figure 2.2B). These vessels discharged to a smaller 440 L HDPE reservoir where air stripping was implemented as a final precaution before the treated water was released to a municipal drain via a submersible pump. Both treatment reservoirs were also hooked up to the custom exhaust system to maintain indoor air quality.

The synthetic groundwater was composed of de-chlorinated tap water amended with a concentrated nutrient stock solution, which was prepared in advance (3.0 L batches) and stored at 4°C. Preparation of the groundwater occurred in the two 1400 L source water reservoirs (Figure 2.3B). In general, 50 mg/L of NH₄NO₃ and K₂HPO₄ were added to provide additional buffering capabilities and essential macronutrients necessary for bacterial growth except for a carbon source. The overall chemical contribution of both the nutrient media and tap water created a groundwater consistent with an unconfined, shallow homogeneous system of insoluble, sandy material with high nitrate loadings.

It should be noted that the nutrients were gradually lowered to 25 mg/L of NH₄NO₃ and 12.5 mg/L of K₂HPO₄ over a 22 day period in late June 2012 (Chapter 3, $PV \approx 12.5$) to reduce the magnitude of excess nutrients discharged to waste. However, these conditions were only maintained for six months before nutrient concentrations were increased step-wise to 50 mg/L of NH₄NO₃ and 25 mg/L of K₂HPO₄ at the end of November 2012 (Chapter 4, t = 93 days) to potentially boost denitrification during biodegradation. Regardless of the nutrient loading, an unexpected consequence of adding NH₄NO₃ to the source water was the autotrophic consumption of dissolved oxygen via microbially-mediated nitrification. O₂ concentrations in the *HTs* ranged from 0.0 to 6.5 mg/L which were less than that of the fresh tap water (typically 8.5 mg/L) but dependent on nutrient loadings and/or applied groundwater velocity. However, no O₂ was detected in

any of the *MWs* following the initial nutrient spike (e.g. after 2.0 *PVs* in Figure 2.4; nearly identical results were observed for all other wells in both lanes). Thus, an up-gradient portion of the aquifer (i.e., before *MW1* located 115 cm from the *HT*) may have been intermittently aerobic when O_2 concentrations were high in the *HTs*, which occurred during the first experiment only (Chapter 3). But in general, anoxic conditions were sustained in the aquifer throughout this dissertation.



Figure 2.4: Early-time changes in dissolved oxygen concentrations (mg/L) from the head tank (blues lines, 0 cm down-gradient) and monitoring well 3 (red and orange lines, 375 cm down-gradient) in Lane 1 at two depths: 60 cm (lighter shade) and 130 cm (darker shade) after inoculation and initial nutrient additions, the start of the first tank experiment (Chapter 3). Note that technical issues prevented reliable data collection prior to $PV \approx 1$.

Hydrocarbon contamination and inorganic tracers could be introduced into each lane through three 4-inch PVC injection wells installed as a fence, located 30 cm down-gradient of the HTs to avoid bioclogging of the geotextile (Figure 2.3A). These wells were fully screened and well mixed by a peristaltic pump. which circulated water from the bottom to the top at a rate 3.3x faster than the total discharge rate out of a lane. Concentrated aqueous hydrocarbon mixtures could be injected below the water surface in each well at a constant rate using a low flow, precision peristaltic pump (see Chapter 4 for more details). In addition, concentrated potassium bromide (KBr; conservative tracer) solutions could be individually added to the injection wells to conduct pulse inorganic tracer tests. In this case, the volume added was minimized (≤ 0.1 L) to reduce artificial spreading of tracer during introduction and the continuous internal circulation effectively distributed the solution throughout each well, creating a uniform pulse input concentration of 1.0 g/L of KBr. Changes in bulk electrical conductivity (refer to *TDR* system for details) captured along each *in situ* instrument array, located set distances down-gradient of the HTs, were used to track the progression of tracer tests. Any tracer test data presented in this dissertation was used for illustrative purposes only.

2.3.1 In situ Instrumentation and Trapped Gas Calculations

In each lane, thirty 30-cm long, three-pronged stainless steel *TDR* probes (Campbell Scientific, Edmonton, Alberta, Canada) were embedded horizontally in the sand and distributed at six different depths (15, 45, 75, 105, 135 and 165 cm

below the sand surface) and along five instrument arrays or transects located 70, 155, 205, 320 and 445 cm down-gradient of the head tanks (0 cm). Every 2 - 6 hours, a Time Domain Reflectometer (TDR100) released a high-frequency electromagnetic pulse to the coaxial system, which consisted of the *TDR* probes (CS605) connected to eleven 50 ohm, eight-channel coaxial multiplexers split across three levels using RG58 cables (Figure 2.5). The TDR100 digitized the resulting reflection waveforms for each probe and applied the internal numerical algorithms following user-specified instructions contained in a CR1000 logger, which was accessed from a personal computer running *LoggerNet* Software (Campbell Scientific). Applied algorithms measured elapsed propagation times and attenuation of the pulse off captured waveforms, which then were used to determine volumetric water content following the empirical relationship of Topp et al. (1980) and bulk electrical conductivity using the Giese-Tiemann Method (Topp et al., 1988).

Trapped gas contents (% of bulk volume) could then be determined for individual *in situ* locations by subtracting the measured volumetric water content (derived from *TDR*) from the tank's bulk porosity value (*n*). Alternately, gas contents could also be calculated by subtracting the measured water content (derived from *TDR*) from the final volumetric water content (also derived from *TDR*), representing a local maximum effective porosity (n_e) following complete dissolution of the gas phase. Both techniques produced very similar results. The latter was more accurate, accounting for local micro-heterogeneity in the sand pack surrounding a given *TDR* probe; however, it could only be applied at select

locations where the trapped gas had fully disappeared, observed as a steady plateau in water content over time (near 0% of the bulk volume).



Figure 2.5: Horizontal installation of *in situ TDR* probes and groundwater samplers during the packing procedure within each lane, 15 cm below the sand surface (A). The *TDR* control center containing: 1) CR1000 logger, 2) reflectometer (TDR100), 3) level 1 multiplexer, 4) battery and 5) barometric pressure sensor (B). Overall *TDR* system including the 10 multiplexers hooked up to the *TDR* probes, split evenly over two additional multiplexer levels (C).

Note for Chapter 3, all continuous volumetric water contents measured after June 2012 ($PV \approx 12.5 - 18.8$) were corrected to account for an apparent increase in entrapped gas content, which was correlated to differences in bulk electrical conductivity induced by amendments in the nutrient loadings (recall Section 2.3). The overall change between original and corrected gas contents ranged from 0.1% to 1.0% and from 0.3% to 0.9% for Lanes 1 and 3, respectively, which falls within the accuracy of *TDR* probes. This is consistent with the findings of Sun et al. (2000), who showed that volumetric moisture contents can artificially vary as a function of bulk electrical conductivity at low soil salinities and quasi-saturated conditions due to slight changes in the resolution or attenuation of the *TDR* signal.

2.3.2 In situ Groundwater Samplers and Analytical Procedures

Each *TDR* probe was coupled with a groundwater sampler (*GWS*) consisting of a 3-inch stainless steel, 40-µm porous cup (Chand Eisenmann Metallurgical, Burlington, Connecticut, USA) connected to stainless steel tubing. They were also embedded horizontally in the sand during packing, 13 cm down-gradient of a *TDR* probe (Figure 2.5A). Designated HDPE 30 mL syringes were used to purge the lines and collect representative groundwater samples, analyzed for aqueous hydrocarbon, nutrient and major ion concentrations (Chapter 4 only). Consequently, during a sampling event, a variety of 20 - 60 mL samples requiring different handling and/or treatments were collected from a

single *TDR* location. Refer to Table 2.2 for groundwater sampling details relative to each analyte type.

Analyte	Container	Sample Treatments	Storage Conditions	Analytical Methods
Hydrocarbons	20 mL, glass vial with mininert valve	No headspace, preserved with 0.1 g of sodium bisulphate	Refrigerated at 4°C for ~14 days	P&T GC-MS
Major Anions	30 mL, HDPE bottle	Filtered through 0.20 µm sterile syringe filter	Refrigerated at 4°C for ~ 30 days	IC
Major Cations	125 mL, HDPE bottle	Filtered through 0.20 µm sterile syringe filter and acidified to pH<2 with 10% nitric acid (HNO ₃)	Indefinite shelf life	ICP-OES
Ammonium	30 mL, HDPE bottle	No headspace , filtered through 0.20 µm sterile syringe filter and acidified to 5 <ph<6 10%="" acid<br="" hydrochloric="" with="">(HCI)</ph<6>	Frozen, indefinite shelf life	UV/Vis-S

Table 2.2: Summary of groundwater sampling details, such as container type, sample treatment, storage and analytical quantification method used.

Hydrocarbon samples were analyzed by Purge and Trap Gas Chromatograph Mass Spectrometry (P&T GC-MS). Samples were diluted prior to being loaded onto a Tekmar 3100 Purge and Trap Concentrator. Individual constituents were separated with an Agilent 6890 Gas Chromatograph on a DB624 (0.25 mm ID, 1.4 µm film thickness and 60 m in length) capillary column. The temperature program involved, heated the oven to 45°C for 3 minutes then ramped up to 90°C and held for 4 minutes following an 8°C/minute increase, and then again ramped at 6°C/minute to 200°C which was held for 5 minutes. Compounds were eluted to an Agilent 5973 Mass Spectrometer for detection in full scan mode from mass 45 to 300 a.m.u. Identification and quantification were performed by comparing retention times and peak areas of mass spectra to those obtained from known standards under identical analytical conditions. An internal standard was used to normalize instrument variation. Calibrations standards were prepared at seven different concentration levels from certified standard solutions. The method detection limits for ethanol, MTBE and toluene were 1.10, 0.10, and 0.10 μ M, respectively.

Major anions were analyzed by Ion Chromatography (IC) using a Dionex 2500 IC system. Anions were separated on a Dionex AS18 column (4 mm x 250 mm) fitted with a Dionex AG18 guard column (4 mm x 50 mm) at a flow rate of 1.0 mL/min at 30°C. Potassium hydroxide (KOH) eluent concentration was held at 22 mM for the first 5 minutes before increasing to 50 mM over 1 minute, which was then held for 16 minutes. Aqueous anion concentrations were determined using a seven point calibration curve based on a solution suite prepared daily from a mixed certified standard solution. The method detection limits for dissolved bromide, chloride, fluoride, nitrite, nitrate, phosphate and sulphate were 0.30, 0.30, 0.20, 0.20, 1.10, 0.20 and 0.50 µM, respectively.

Major cations were quantified using an ULTIMA 2 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) at RF generator power of 1000 W, sample uptake rate of 1.0 mL/min and argon gas/plasma flow of 12 L/min. Element-specific wavelength intensities were compared to measured intensities of known standard concentrations (7 concentration levels total) which were prepared fresh from certified standard solutions. The method detection

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limits for dissolved aluminum, calcium, iron, potassium, magnesium, manganese, and sodium were 1.20, 0.50, 0.40, 3.00, 0.25, 0.50 and 0.20 µM, respectively.

Prior to analysis, ammonium samples were thawed, mixed and subsampled. A standard phenol and hypochlorite reaction producing indophenol blue was measured using a Beckman Coulter DU 720 UV/Vis Spectrophotometer equipped with a 1 cm flow through cell. Indophenol blue absorbance was measured at 640 nm as directed by Solorzano (1969) and related to nitrogen (N) concentration as ammonium using a seven point calibration curve based on standards prepared daily from an ammonium chloride solution. The method detection limit for ammonium was 1.50 µM.

2.3.3 Monitoring Well Equipment

Three 4-inch PVC monitoring wells screened over two depth intervals (Figure 2.6A) were located along the flow path, 115 cm, 250 cm and 375 cm down-gradient of head tanks in the each lane. These wells hosted two sets of passive gas samplers (*PGS*, used in Chapter 4 only), luminescent dissolved oxygen (*DO*) sensors, and total dissolved gas pressure (P_{TDG}) probes at 60 cm (upper) and 130 cm (lower) below the sand surface to capture changes in dissolved gas conditions (Figure 2.6). Upper and lower halves of the monitoring wells were isolated using thin custom baffles of red prime rubber to prevent vertical flow through the wells. The *PGS* were assembled using gastight glass syringes (500 µL; VICI-Valco Instruments, Brockville, Ontario, Canada) and 8.5 cm sections of gas-permeable silicone tubing (ID 1/8") according to the

procedures described by Spalding and Watson (2006) (Figure 2.6C). These samplers were filled with atmospheric air prior to being secured to the *DO* probes and installed into the monitoring wells. The same configuration of monitoring well equipment was also placed in the open head tanks to monitor the source water.



Figure 2.6: The cross-sectional profile (A) of a monitoring well where dissolved oxygen (*DO*) sensors, total dissolved gas pressure (P_{TDG}) probes (B) and passive gas samplers (*PGS*, C) were hung at two vertical positions (approximately 60 cm and 130 cm) and separated by packers (red disks). Hatched sections correspond to screened intervals of wells.

DO probes (HACH Company, Loveland, Colorado, USA) were connected to modules with a sc1000 Digital Controller to record groundwater temperature (°C) and dissolved oxygen concentrations (mg/L) every 30 min. P_{TDG} probes (Figure 2.6B, Point Four Systems, Coquitlam, British Columbia, Canada) were wired to 21X Microloggers (Campbell Scientific) to acquire hourly pressure readings (kPa) based on user-defined *EdLog* instructions. The *PGS* were used to collect gas in equilibrium with groundwater for measurement of dissolved gas composition (i.e., the abundance or percent of N₂, O₂, CO₂, CH₄ and H₂ by volume) roughly every 60 days. Duplicate *PGS* measurements were quantified by gas chromatography. All monitoring well equipment was pulled up for probe maintenance every 30 to 60 days, which included cleaning and sensor cap or cartridge replacement.

The *PGS* syringes were injected directly onto 8610C SRI Gas Chromatograph (GC) using a 10 port switching valve. Sequential analysis of the dissolved gas analytes used a thermal conductivity detector (TCD), and a helium ionization detector (HID). This instrument was equipped with a silica gel packed column (6-ft long) in series with a mesh column (6-ft long x 1/18" Molecular Sieve 13X 80/100) and a helium carrier gas at a flow rate of 20 mL/min. The analytical method controlled the initial instrument temperature at 30°C for 3 minutes before increasing the temperature gradient at a rate of 20°C/min to 40°C for 1 minute. The temperature was then ramped up at 8°C/min to 120°C and held for 0.1 minute before increasing again 40°C/min to 150°C for 5 minutes. Identification and quantification of each gas analyte was performed by comparing retention times and peak areas to those obtained from known standards run under identical conditions. Calibrations standards were prepared at room temperature and ambient atmospheric pressure using several high-purity gas cylinders. These high-purity gas standards were also diluted with helium using a syringe (gastight) technique (see McLeish et al. 2007) in order to prepare standard samples with differing concentrations to create three to seven point calibration curves for each analyte. Note all *PGS* data (except CH₄ values from *t* = 300 days) presented were based on HID derived results since TCDs are less sensitive to low gas concentrations. Refer to Table 2.3 for the complete set of calibration statistics, including quantification limits, for the HID-GC analytical system used.

Gas Species	Mean R ² Values ^a (± 2STDEV)	Mean RSD between Duplicates ^b (%)	Quantification Limits (% by Volume)
N ₂	$\textbf{0.978} \pm \textbf{0.047}$	1.67%	0.50
O ₂	$\textbf{0.991} \pm \textbf{0.010}$	7.77%	0.50
CO ₂	$\textbf{0.993} \pm \textbf{0.015}$	5.03%	0.05
CH ₄	0.993 ± 0.007	3.10%	0.05
H ₂	$\textbf{0.997} \pm \textbf{0.004}$	5.98%	0.10

Table 2.3: Calibration statistics for the analytical system, a SRI Gas Chromatograph equipped with a Helium Ionization Detector, used for Passive Gas Sampler analysis.

^a Mean coefficient of determination (R²) of the least squared linear regressions relating standard analytical responses to known standard concentrations (calibration curves) for each gas species.

^b Mean relative standard deviation (RSD) of all duplicate samples, representing the precision and repeatability of duplicate measurements.

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CHAPTER 3

Patterns of entrapped air dissolution in a two-dimensional pilot-

scale synthetic aquifer

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3.1 Introduction

It has been well known for the past 70 years that water table fluctuations can entrap atmospheric air and/or soil gas as a discontinuous gas phase within the capillary fringe and even below the groundwater table, thereby creating a zone of guasi-saturation (Smith and Browning 1942; Christiansen 1944). This can occur naturally, as a result of evapotranspiration, infiltration, or groundwatersurface water interactions, or it can be caused by groundwater resource exploitation. Substantial gas phase saturations up to 54% of the pore space have been reported following water table fluctuations (see Marinas et al. 2013; and references therein), although this can vary significantly with the soil type and grain size distribution (Constantz et al. 1988; Fry et al. 1997), the rate of infiltration and initial soil moisture content (Fayer and Hillel 1986a, 1986b), and pore structure or geometry (Peck 1969; Fry et al. 1997). It can be further enhanced by the presence of heterogeneity and/or air entry barriers (Dunn and Silliman 2003). Furthermore, entrapped gas saturations tend to decline with depth below the water table due to compression at increasing water pressures (Marinas et al. 2013).

An entrapped gas phase may also form *in situ* where dissolved gases are being produced by biogeochemical processes, such as in wetlands (e.g. Baird et al. 2004) or at sites with groundwater contamination (e.g. Amos et al. 2005). In addition, entrapment can follow groundwater remediation techniques that inject gases (e.g. air sparging; Balcke et al. 2007, 2011), or gas-supersaturated waters (Enouy et al. 2011). While the focus in this study was on entrapped air following

water table fluctuations, it is expected that the key findings will also be applicable to these other cases of discontinuous trapped gas.

Gas trapped within a porous (or fractured) medium tends to fill the largest pores, effectively reducing the saturated hydraulic conductivity by a factor of 2 -20 (Marinas et al. 2013 and references therein). Such reductions can decrease natural and artificial groundwater recharge (Christiansen 1944; Constanz et al. 1988; Faybishenko 1995; Heilweil et al. 2004) and/or create stagnant flow zones (Ryan et al. 2000), which can impede solute, contaminant and microbial transport within the vicinity of the groundwater table (Orlob and Radhakrishna 1958; Berkowitz et al. 2004; Amos and Mayer 2006). Interactions with entrapped air can also affect groundwater biogeochemistry and contaminant transport. For instance, entrapped air can supply dissolved oxygen for contaminant biodegradation (Williams and Oostrom 2000; Holocher et al. 2003; Haberer et al. 2012) or retard the transport of dissolved gas tracers (i.e., chlorofluorocarbons, Helium and SF₆) in groundwater (e.g. Donaldson et al. 1998; Cirpka and Kitanidis 2001; Clark et al. 2005). Also, preferential partitioning of volatile compounds from non-aqueous phase liquids (NAPLs) into entrapped air can cause spontaneous growth and movement of the residual gas phase, thus affecting contaminant mass transfer in NAPL source zones (Roy and Smith 2007). In addition, the dissolution of entrapped air can have implications for paleoclimate studies using noble gas infiltration or recharge temperatures (e.g. Aeschbach-Hertig et al. 2000).

Entrapped air tends to dissolve into the aqueous phase over time because passing groundwater is typically under-saturated with dissolved gases compared to the pressure of the trapped gas phase. In fact, higher trapped gas phase pressures occur at greater water pressures (i.e., depth below the water table) and induce faster dissolution (Holocher et al. 2003). As a result of this dissolution, groundwater can achieve supersaturation of dissolved gases with respect to atmospheric equilibrium, a widespread phenomenon known as 'excess air' (Heaton and Vogel 1981). Previous studies on entrapped air dissolution have largely focused on the formation and fractionation of excess air using a variety of gas-water exchange models (e.g. Kipfer et al. 2002; Aeschbach-Hertig et al. 2008), with experimental work largely restricted to small-scale (\leq 1.0 m), onedimensional systems where the influence of hydrostatic pressure on entrapped air dissolution was discussed (Holocher et al. 2002, 2003; Geistlinger et al. 2005; Klump et al. 2008).

The main objective of this study was to investigate the multidimensional nature of entrapped air dissolution under horizontal flow conditions and its implications for groundwater flow and dissolved solute transport, which has not been addressed to date. It was expected that depth-dependent effects on mass transfer from entrapped air and on quasi-saturated hydraulic conductivity would lead to a temporally and spatially variable dissolution pattern. Experiments were performed in a highly instrumented, large-scale laboratory tank simulating an unconfined sand aquifer. *In situ* Time Domain Reflectometry (*TDR*) probes directly captured changes in the entrapped gas saturation following air

entrapment via a water table fluctuation. Dissolved gas conditions were monitored using dissolved oxygen sensors and total dissolved gas pressure (P_{TDG}) probes. A secondary objective of this study was to test the effectiveness of P_{TDG} probes for monitoring the presence and dissolution of entrapped air, as previously proposed by Manning et al. (2003).

3.1.1 Relevant Background on Entrapped Air Dissolution

A brief synopsis of trapped gas dissolution and some of its controlling factors is provided here; for a rigorous description refer to Holocher et al. (2003). When water is in contact with a gas phase, mass will be exchanged across the gas-water interface to establish equilibrium between the phases. At equilibrium, for a given gas *i*, its partial pressure in the gas phase (p_{gi}) is related to its dissolved concentration (C_{gi}), as described by Henry's Law:

$$K_{Hi}(T,S) = \frac{\rho_{gi}}{R \cdot T \cdot C_{gi}}$$
(1)

where *R* is the universal gas constant, *T* is the absolute temperature, and K_{Hi} is the gas' dimensionless Henry's Law proportionality coefficient, which is dependent on the prevailing temperature (*T*) and salinity (*S*). It is apparent from Equation 1 that an increase in p_{gi} will induce mass transfer from the gas phase into the groundwater (i.e., dissolution) and a subsequent increase in C_{gi} , or vice versa.

Dissolution of entrapped air is more complicated when multiple gases are involved. Mass transfer of different gases may occur in opposite directions according to Equation 1 and the specific K_{Hi} and p_{gi} of each gas. However, these will be coupled through Dalton's Law, which states that the total pressure of the trapped gas phase (P_G) is equal to the sum of all the partial pressures of the gases present in it, that is,

$$\boldsymbol{P}_{G} = \sum \boldsymbol{p}_{gi} \tag{2}$$

It is also apparent from Equations 1 and 2 that dissolution of all the gases will be consistently influenced by changes to P_{G} , which can be affected by a number of external forces, according to

$$\boldsymbol{P}_{G} = \boldsymbol{P}_{w} + \boldsymbol{P}_{c} = \left(\boldsymbol{P}_{atm} + \boldsymbol{\rho} \cdot \boldsymbol{g} \cdot \boldsymbol{h}\right) + \left(\boldsymbol{\sigma}\left(\frac{1}{r_{1}} + \frac{1}{r_{2}}\right)\right)$$
(3)

where P_w is the water pressure, which is a function of barometric pressure (P_{atm}) and the density of water (ρ), the acceleration due to gravity (g), and the depth below the water table (h) under hydrostatic conditions; and P_c is the capillary pressure, which is related to the surface tension of water (σ) and the curvature of gas-water interfaces (where r_1 and r_2 represent the principal radii of curvature of the trapped gas ganglia) according to the Young-Laplace Equation. As a result, P_G for trapped gases and thus, the potential for dissolution, will increase with depth below the top of the capillary fringe (and also the water table; Collis-George and Bond 1981; Dunn and Silliman 2003). Furthermore, the contribution of P_w is expected to dominate over that of P_c for coarse-grained aquifers, given the expected radii of the gas-water interfaces. Consequently, P_c is commonly ignored or assumed to be negligible (Manning et al. 2003; Klump et al. 2007, 2008); though neglecting P_c may underestimate the potential for dissolution. Frequently, the passing groundwater is assumed to be in equilibrium with the atmosphere, which is true for infiltrating water where the sum of partial pressures of the dissolved gases is equal to the prevailing P_{atm} . Consequently, it is also clear from Equation 3 that the dissolution of entrapped air at even minimal P_w (i.e., shallow depths below the water table) will be favoured when first contacted by water. However, upon fully equilibrating with entrapped air, groundwater under strict horizontal flow conditions will no longer drive trapped gas dissolution down-gradient (Klump et al. 2008).

Total dissolved gas pressure (P_{TDG}) probes measure the sum of the partial pressures of the dissolved gas species (Manning et al. 2003), effectively capturing the net influence of the dissolved gas concentrations. As a result, field P_{TDG} readings, representing the condition of the dissolved gases, can be compared with the expected P_G for a given depth and porous medium following Equation 3, to assess whether entrapped air is undergoing dissolution ($P_G > P_{TDG}$) or whether the two phases are in local equilibrium ($P_G = P_{TDG}$).

3.2 Methods

3.2.1 Experimental Set-up

The pilot-scale synthetic aquifer was assembled using approximately 36.5 metric tonnes of medium silica sand (designation: BARCO M49, Opta Minerals Inc., Waterdown, Ontario, Canada) in a stainless steel tank (600 cm long × 240 cm wide × 180 cm deep; Figures 3.1 and 2.3) located at the Canada Centre for Inland Waters in Burlington, Ontario, Canada. The average overall porosity (n) of

the packed tank was 37.6%. The tank was divided lengthwise into three separate test lanes, each 80 cm wide and each with an open reservoir head tank (*HT*, 80 cm wide × 75 cm long) located at one end and separated from the aquifer (i.e., sand-packed section) by a steel perforated plate affixed with a non-woven polypropylene geotextile (Nilex, Toronto, Ontario, Canada). Only the two outside lanes (Lanes 1 and 3) were used in this study (Figure 2.3A); these were packed to be homogeneous. Further details on sand properties including the nature of the quasi-saturated hydraulic conductivity (K_{qs}) as a function of trapped gas saturation (Figure 2.1) and on packing procedures are provided in Chapter 2.

The synthetic groundwater used for this experiment was composed of dechlorinated tap water amended with a concentrated nutrient stock solution (see Chapter 2). The water was gravity fed into the head tanks, which were equipped with industrial brass float valves in order to maintain the up-gradient constant head boundary conditions. Groundwater flow was generated by pumping with a peristaltic pump from one fully screened 4-inch PVC withdrawal well centered at the end of each lane, 520 cm from the *HTs* (Figure 3.1 and 2.3). Note that the withdrawal well rates (i.e., the flow velocities) changed during the experiment, as outlined below in Section 3.2.2. A pore volume (*PV*) was calculated as the water volume within the sand-filled section of one lane (1 *PV* = 2760 L).

In each lane, thirty 30-cm long, three-pronged stainless steel Time Domain Reflectometry (*TDR*) probes (Campbell Scientific, Edmonton, Alberta, Canada) were embedded horizontally in the sand during packing (Figure 2.2). These probes were distributed at six different depths (15, 45, 75, 105, 135 and

165 cm below the sand surface) and along five instrument arrays or transects located 70, 155, 205, 320 and 445 cm from the *HT*s (0 cm) (Figure 3.1). *TDR* waveforms from each probe were collected at 2 h to 6 h intervals and interpreted with the empirical relationship of Topp et al. (1980) to compute volumetric moisture contents. Complete details of the *TDR* data acquisition system are provided in Chapter 2.



Figure 3.1: The cross-sectional profile (A) and plan view (B) of the experimental design for each individual lane used in the pilot-scale tank. The dotted line represents the sand surface whereas the solid blue roughly represents the position of the water table. Ambient groundwater flow occurred from left to right; from head tank (*HT*) to withdrawal well where hatched sections correspond to screened intervals of wells. Dissolved oxygen (*DO*) and total dissolved gas pressure (P_{TDG}) probes (red stars) hung in the *HTs* (0 cm) and three monitoring wells (*MW1*, *MW2*, and *MW3*), located 115, 250 and 375 cm down-gradient, at two vertical positions (60 and 130 cm) separated by packers. *TDR* probes were distributed at 6 vertical depths below sand surface (15, 45, 75, 105, 135 and 165 cm) along five in situ instrument arrays (in green) located 70, 155, 205, 320, and 445 cm down-gradient of *HT*.

Entrapped air contents (% of total bulk volume) were calculated by subtracting measured volumetric water contents at a given location from a maximum effective porosity (n_e). The n_e values were approximated as the highest volumetric water contents observed after complete trapped gas dissolution or else as the overall calculated bulk porosity (n). These trapped gas calculations are described in Chapter 2; however the choice of method did not significantly affect the results. Soon after the start of the experiment, technical problems with the *TDR* operating system prevented continuous measurements for several extended periods until January 2012 ($PV \approx 2.0$). In addition, all volumetric water contents measured after June 2012 ($PV \approx 12.5$) were corrected to account for an apparent increase in entrapped air content associated with a decrease in bulk electrical conductivity caused by lower nutrient amendments (refer to Chapter 2).

Three 4-inch PVC monitoring wells (*MW*) screened over two depth intervals were located along the flow path at 115, 250, and 375 cm from the *HT* in each lane (Figure 3.1 and 2.6). These wells hosted two sets of luminescent dissolved oxygen (*DO*) sensors and total dissolved gas pressure (P_{TDG}) probes at approximately two depths, 60 cm (upper) and 130 cm (lower) below the sand surface. Upper and lower halves of the monitoring wells were isolated by thin custom rubber baffles to prevent vertical flow in the wells. The same configuration of monitoring well equipment was also placed in the open *HT* to monitor the source water. *DO* sensors (HACH Company, Loveland, Colorado, USA) recorded dissolved oxygen concentrations (mg/L) and groundwater temperature (°C) every 30 minutes; while P_{TDG} probes (Point Four Systems Inc., Coquitlam, BC, Canada) recorded hourly pressure readings (kPa). All probes were removed every 30 - 60 days for maintenance.

3.2.2 Experimental History of Tank

Following packing, all lanes were fully wetted in July 2010 with tap water (always de-chlorinated). Over the next 12 months, the tank was used for other purposes, for which approximately 8.2 pore volumes were passed through Lane 1 during intermittent use. Lane 3 was partially drained and remained not in use until May 2011 when it was flushed with 2.0 pore volumes of tap water. Subsequently, in preparation for the present study, the entire system was slowly drained until the water level in the *HT*s was 2 cm from the bottom. However, within the sand-filled tank, the capillary fringe remained (~26 cmH₂O; Table 2.1), ultimately preventing the re-introduction of air into the bottom section. In September 2011, the system was re-wetted over two days with a sprinkler system from the sand surface (top), simulating a 155 cm rise in the water table during recharge.

Consequently, the initial condition for the present study consisted of two zones of quasi-saturation, one from the sand surface to a depth of ~150 cm and one from ~150 cm to the tank bottom. The main difference was that the lower zone experienced some dissolution from July 2010 to September 2011, while the upper section had the entrapped air re-set for the start of this experiment. The extended dissolution in the lower zone only affected *TDR* data at the 165 cm monitoring depth. This initial condition is still representative of a natural

unconfined aquifer because any given water table oscillation will infrequently cover the maximum depth over which the water table may fluctuate; thus creating vertical zonation that has experienced varying degrees of dissolution. In addition, the simulated water table fluctuation was realistic because numerous field studies have documented the existence of trapped atmospheric air in the (quasi-) saturated zone up to several meters deep (Christiansen 1944; Fayer and Hillel 1986a, 1986b; Constantz et al. 1988).

For the present study, the final position of the water table was established \sim 10 cm below the sand surface, thus saturating (except for entrapped air) the entire aguifer thickness, in part by capillary rise. Flow was initiated at an average linear pore water velocity of 10.4 cm/day at the end of September 2011 (PV = 0.0) using synthetic groundwater rather than pure tap water. After 0.9 pore volumes passed (mid-December 2011), groundwater flow was increased to 54.3 cm/day. For one month (March to April 2012; PV = 7.2 to 8.1; a result of technical problems) a smaller average velocity of 22.6 cm/day was used, before increasing back to 54.3 cm/day. Subsequently, in mid-July 2012 (PV = 14.7), in preparation for future tank work, the seepage velocity in Lane 1 was dramatically increased to 105.0 cm/day while the velocity in Lane 3 was concurrently decreased to 23.0 cm/day until the conclusion of the experiment in August 2012. In total, 18.8 and 16.5 pore volumes were passed through Lanes 1 and 3, respectively, over approximately 344 days. All data have been plotted relative to cumulative pore volumes passed rather than time, to account for these changes in discharge rates and short-term no-flow conditions during equipment maintenance. The velocity changes could have affected dissolution rates locally, but such changes are not expected to influence the general pattern of dissolution.

3.3 Results and Discussion

3.3.1 Initial Entrapped Air Distribution and Mechanisms Influencing Dissolution

The initial entrapped air contents at the start of *TDR* measurements (seven-day average; PV = 0.0) ranged from 0.0% to 7.1%. In general, the distribution of air contents was similar for both lanes, but is only illustrated for Lane 1 in Figure 3.2A. The entrapped air contents observed at the 15 cm depth ranged from 6.1% to 6.8% and 5.8% to 7.1% in Lanes 1 and 3, respectively. These represent average trapped gas saturations (air content divided by overall porosity) of approximately 16.9% to 17.4%. This is very consistent with residual gas saturations reported in the literature for coarse-grained sand as a result of water table fluctuations (Marinas et al. 2013; and references therein). Lower entrapped air contents measured along the bottom of each lane, ranged from 0.0% to 2.8% and 0.4% to 5.0% for Lane 1 and 3, respectively, and were a consequence of earlier dissolution during work prior to this study (refer to Section 3.2.2).

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Figure 3.2: Cross-sectional distributions of entrapped air contents (% of total volume) within Lane 1: A) following the water table fluctuation (PV = 0.0); B) at PV = 8.6; and C) at the end of the experiment (PV = 18.8). Symbols mark the locations of the *TDR* probes. Interpolated from daily *TDR* averages using a radial basis multi-quadric function and default R2 shaping factor (220) in Surfer Software (Golden Software Inc., Golden, Colorado, USA); it is not an exact interpolator but provides smoother contours.

Excluding the bottom *TDR* row, initial entrapped air contents steadily decreased with depth (Figure 3.2A), with average reductions in gas saturations of 27% between depths of 15 cm and 135 cm in both lanes. This reflects increasing

compression of the trapped gas phase with greater P_w at depth (Holocher et al. 2003; Marinas et al. 2013). These initial entrapped air data were plotted against P_w in Figure 3.3, along with the results of two small-scale, 1-D column experiments, which followed the methods of Marinas et al. (2013) but used the same BARCO M49 sand as in the tank (see Chapter 2). On average, both lanes exhibited linear decreasing trends in entrapped air contents with increasing water pressure, with slopes of -1.3×10^{-2} and -1.1×10^{-2} (% of total volume cmH₂O⁻¹) for Lanes 1 and 3, respectively. These are similar to the results of the BARCO M49 sand 1-D column tests (-9.3×10^{-3} and -5.4×10^{-3} % of total volume cmH₂O⁻¹, with an offset for Trial A due to a higher initial air entrapment) and the maximum slopes (-1.2×10^{-2} to -1.4×10^{-2} % of total volume cmH₂O⁻¹) reported by Marinas (2009) for other sands. There was significantly more variation present in the tank results, with lower R-squared values of the linear regressions, i.e., 0.81 (Lane 1) and 0.79 (Lane 3), than observed in the BARCO M49 sand columns, which had R-squared values >0.95, consistent with regression results of Marinas (2009). It is likely that heterogeneities created during the large-scale packing of the tank, although minor compared to the natural environment, generated more variable initial entrapped air distributions than observed in the small-scale, 1-D column experiments.

In the presence of entrapped air, the Darcy coefficient of water conductivity is lower than the saturated hydraulic conductivity (K_s) and referred to as the quasi-saturated hydraulic conductivity (K_{qs}) (Faybishenko 1995). The relative hydraulic conductivity ($K_r = K_{qs}/K_s$) for the initial conditions in the tank

were estimated from K_r vs. entrapped air saturation data from the 1-D column tests with the BARCO M49 sand and relevant data from Marinas et al. (2013) (Figure 2.1). The resultant K_r values ranged from 0.67 at 15 cm depth to 0.76 at 135 cm depth. Therefore, a 12% difference in K_{qs} was estimated to exist across this 120 cm depth range, which should favour dissolution at depth, as suggested by Holocher et al. (2003). In addition, the estimated K_{qs} values were even lower along the bottom of each lane, denoted here as higher K_r values: 0.77 (Lane 3) and 0.87 (Lane 1), due to the prior dissolution mentioned above.



Figure 3.3: Entrapped air content vs. water pressure (or depth below the water table) relationships for Lane 1 (blue diamond) and Lane 3 (red square) of the pilot-scale tank, and for two 1-D column tests (open circles and triangles) using the BARCO M49 sand (see Chapter 2). Tank data represent averaged values of all five *TDR* transects at a given depth, except for 155 cmH₂O, for which none and 2 transects were included for Lane 1 and 3, respectively, because the rest were affected by previous dissolution. Error bars represent one standard deviation. Lines represent least squares linear regression results with corresponding R² values for each dataset.

Following the initiation of groundwater flow, the early-time P_{TDG} measurements in the aquifer for both lanes and all wells were quasi-constant at approximately 105 and 112 kPa for the 60 and 130 cm depths, respectively, though they fluctuated with changes in P_{atm} , as depicted in Figure 3.4 for Lane 1. In fact, all of the P_{TDG} measurements closely mimicked P_w (= P_{atm} + ρgh ; Equation 3), which is also equal to the expected local P_G of trapped gases at these same locations under negligible capillary pressures (Equation 3). This is also the expected value of the bubbling pressure (P_{G}^{*}) , the dissolved gas pressure at which a gas phase is expected to form, ignoring any nucleation energy thresholds (i.e., pre-existing seed bubbles are present in the medium) (Jones et al. 1999). These observations of P_{TDG} readings equal to P_{G}^{*} despite changing P_{atm} (Figure 3.4), indicate that equilibrium was reached between the entrapped air and dissolved gases in the passing groundwater (Manning et al. 2003). In contrast, P_{TDG} of the source groundwater in the open HTs, where no entrapped air existed, were nearly identical at both depths and were lower than the relevant bubbling pressures and atmospheric equilibrium, due to the loss of oxygen in the HTs (Figure 2.4; refer to Chapter 2 for explanation). Consequently, the source groundwater was significantly under-saturated with respect to dissolved gases compared to the local trapped gas phase (i.e., $HT P_{TDG} < P_{atm} <$ P_{G}^{*} in Figure 3.4), which favored dissolution of entrapped air where the source water entered the tank. Furthermore, the dependence of P_{TDG} on P_w as described above, results in a greater driving force for dissolution with depth within the

aquifer, which was also observed in the vertical sand column experiments of Holocher et al. (2003) and Geistlinger et al. (2005).



Figure 3.4: Early-time changes in total dissolved gas pressure (P_{TDG}) for Lane 1, for the head tank (blue lines, 0 cm down-gradient) and monitoring well 3 (red and orange lines, 375 cm down-gradient) at two depths: 60 cm (lighter shade) and 130 cm (darker shade). Also shown are the barometric pressure (light gray line, P_{atm}) and the theoretical bubbling pressures (dark grey line = 60 cm depth, black line = 130 cm depth, P_{G}). Note that technical issues prevented reliable data collection prior to $PV \approx 1$.

3.3.2 Observed Dissolution Pattern

With time (or cumulative *PV* passed), entrapped air contents declined from the head tanks down-gradient (as shown for Lane 1 only in Figure 3.2; but a similar pattern for Lane 3 was observed). This characteristic propagation of the dissolution front along the groundwater flow direction has been seen in both vertical (Holocher et al. 2003; Geistlinger et al. 2005) and horizontal (Klump et al. 2008) 1-D laboratory sand column experiments. It is due to the constant inflow of source water that is under-saturated with respect to the local trapped gas pressure (Holocher et al. 2003). A front occurs because the passing groundwater receives mass from dissolving entrapped air in the up-gradient quasi-saturated zone, elevating groundwater P_{TDG} above background levels towards the P_G^{*} (as seen in Figure 3.4); which then retards the dissipation of the trapped gas phase at down-gradient locations (Klump et al. 2008).

Furthermore, the dissolution front advanced faster at greater depths (Figure 3.2), preferentially spreading the boundary between saturated and guasisaturated conditions across the bottom of both lanes. In fact, at any given TDR array (set distance from the HT), trapped gas contents declined and achieved complete dissolution first at greater depths. Consequently, a wedge-like dissolution front slowly propagated down-gradient and up through the aquifer's thickness over time (Figure 3.2C). Two complementary mechanisms, both associated with the compression of the entrapped air phase with greater P_w at depth, were most likely contributing to this two-dimensional dissolution pattern. The first was an increased rate of mass transfer resulting from pressuredependent changes in gas solubility, as demonstrated in the higher P_{TDG} measurements for the deeper monitoring probe (Figure 3.4). The second was a greater flux of groundwater at depth and thus, a greater dissolution volume over time due to higher K_{qs} with depth, as calculated above (Section 3.3.1). The relative contribution of each mechanism will be discussed further.

Linear propagation of the dissolution front down-gradient was observed at all monitoring depths in both lanes over the duration of the experiment (solid lines, Figure 3.5 for Lane 3; similar results were observed for Lane 1). The position of the front was estimated as the mid-point between initial and final entrapped air contents or P_{TDG} at each TDR or P_{TDG} probe, respectively. The observed linearity of the front propagation provides evidence that the degree of flow line refraction or deflection at the saturated-guasi-saturated boundary was not large enough to alter the flux of groundwater through the aquifer at any depth. In essence, the system behaved like a vertical stack of individual, 1-D. horizontal sand columns (Klump et al. 2008), with increasing rates of propagation with depth. Note that the rate of propagation was guantified here by the slope of the best-fit linear regression line (Figure 3.5) forced through the origin (i.e., front starts at the HT at all depths) (see Table A3.1 for corresponding slopes and R^2 values of regression results). It may be that deviations from linear propagation would occur for porous materials with a greater K_r (K_{as}/K_s), such as finer-grained sediments (Marinas et al. 2013; and references therein). Or, more likely this might occur in the presence of macro-heterogeneity, leading to dissolution fingering; however, further work is required to address this hypothesis.

The propagation of the dissolution front mentioned above was determined using the total discharge rate out of each withdrawal well (i.e., overall bulk flow; solid lines of Figure 3.5). This assumes equal PV passed for all depths, although in reality it was expected that greater flow occurred deeper in the tank due to the increased K_r . To account for this depth-dependent flow, propagation trends were



Figure 3.5: Down-gradient position of the centre of the dissolution front in Lane 3 at each depth below the sand surface, based on *TDR* data: 15 cm (dark green diamonds), 45 cm (light blue squares), 75 cm (green triangles), 105 cm (blue diamonds), 135 cm (light green squares) and 165 cm (navy blue circles); and on P_{TDG} data: 60 cm (orange circles) and 130 cm (red triangles). Data was plotted against bulk average cumulative pore volume passed, based on the total discharge rate. Symbol error bars show 95% confidence interval; solid lines represent least squares linear regressions results for this data (see Table A3.1 for corresponding slopes and R² values of regressions). For comparison, data was scaled for depth-dependent groundwater flux differences (i.e., true number of pore volumes passed at each depth), based on an estimate of the initial K_{qs} profile; the resultant linear regression results are plotted as dashed lines (data points not shown) (see Table S3.1 for *q*-scaled slopes of linear regressions).

scaled according to the relative difference in K_r with depth, determined from the initial entrapped air profile and assuming steady-state flow conditions (i.e., constant hydraulic gradient). Temporal changes to this profile due to entrapped air dissolution were ignored. These results are represented by the dashed best-fit linear regression lines in Figure 3.5. The differences in slopes between the solid

and dashed lines (see Table A3.1) indicate that the enhanced groundwater flux due to P_w -induced compression of the entrapped air did have a small effect on the dissolution front. However, if it was the dominant mechanism controlling the variation in the dissolution front velocity with depth, then all the dashed lines would plot together at some average slope in Figure 3.5. This was not the case, which suggests that the depth-dependence of dissolved gas solubility contributed predominantly to the observed 2-D pattern of entrapped air dissolution.

The observed wedge-shaped dissolution pattern (Figure 3.2 and 3.5) was partly an artifact of the applied boundary condition; that is, the forced horizontal flow regime. In fact, it is expected to differ under conditions with a significant vertical flow component, especially for recharge from the surface with waters potentially in equilibrium with P_{atm} . In this case, based on the results of Holocher et al. (2003) and Klump et al. (2008), it is expected that entrapped air dissolution will be enhanced at shallow depths compared to the pilot-scale tank results. In contrast, persistence of entrapped air in shallow groundwater zones will tend to be enhanced in groundwater discharge areas due to pressure-dependent decreases in gas solubility at smaller P_w encountered during groundwater rise (Geistlinger et al. 2005; Klump et al. 2008). Although this experiment neglected potential complexities associated with vertical flow components, its near fieldscale and multidimensional nature extends the current understanding of entrapped air dissolution in natural porous media where groundwater flow is predominantly horizontal.

3.3.3 Persistence of Entrapped Air

It was possible to roughly and comparably estimate the time required to advance the dissolution front to the end of the tank, 525 cm total, using the linearity of the observed down-gradient propagation (Figure 3.5). For example, at 15 cm depth, near the water table position, 12.9 - 14.3 years would be required for complete dissolution within the sand tank, assuming an average linear pore water velocity of 10.0 cm/day. That is a decade longer than the time required at 165 cm depth. The dissolution of entrapped air within the capillary fringe is expected to be even less favorable because $P_w < 0$. In addition, these estimates could increase considerably with higher residual gas saturations, greater initial dissolved gas loadings of the influent solution and/or lower flow velocities. In contrast, recharge from surface could shorten the estimated life spans of entrapped air at shallow depths and close the depth-induced difference in its persistence. Ultimately, entrapped air within the shallow groundwater zone may persist for a great many years under horizontal flow conditions, which is consistent with the field observations of Ryan et al. (2000) regarding the persistence of a stagnant flow zone around the water table.

3.3.4 Nature of the Dissolution Front

Continuously monitored entrapped air contents, as seen in Figure 3.6 for Lane 3, were all stable with cumulative pore volumes passed until declining with the onset of dissolution at each location. This was consistent with the evolution of gas saturations modeled by Klump et al. (2008) for the case of horizontal flow where dissolution in the up-gradient quasi-saturated zone promoted the persistence of down-gradient trapped gas. However, captured reductions in air contents were more dynamic and did not exhibit monotonically increasing rates of dissolution with time as seen in the theoretical modeling results of Holocher et al. (2002, 2003) and Klump et al. (2008). In fact, the dissolution rates often declined, and in some cases temporarily ceased, in the middle of the dissolution process before entrapped air contents asymptotically approached zero (or water-saturated conditions). In addition, the onset of dissolution at many monitoring points occurred prior to the complete disappearance of entrapped air at corresponding up-gradient locations (Figure 3.6).

These observations reveal a diffuse, rather than a sharp dissolution front, as is commonly reported in the literature based on numerical modeling results. To date, numerical models describing entrapped air-water partitioning under advective-dispersive flow regimes have considered both instantaneous gas transfer (e.g. local equilibrium model of Cirpka and Kitanidis (2001)) or boundary layer kinetics of entrapped gas dissolution in ideal homogeneous porous media (e.g. kinetic bubble dissolution model of Holocher et al. (2003)). However, the pilot-scale tank results suggest that local equilibrium dissolution was not achieved at the meter-scale. It is suspected that additional inter-phase mass transfer kinetics associated with minor heterogeneity in entrapped gas saturations and local K_{qs} were responsible for the observed tailing of the trapped gas extinction curves in Figure 3.6. Similar kinetic effects have been extensively studied in the past with respect to dissolution of residual non-aqueous phase

liquid (NAPL) contamination (e.g. Miller et al. 1990; Powers et al. 1992; Imhoff et al. 1994; etc).



Figure 3.6: Evolution of continuous entrapped air contents (% of total volume) from Lane 3, 135 cm below sand surface at each down-gradient position: 70 cm (navy blue), 155 cm (light green), 205 cm (blue), 320 cm (dark green) and 445 cm (light blue). Note that the resolution of the *TDR* system was lower for short periods at $\sim PV = 5.0$ and 6.0, resulting in less signal noise.

For example, periods of apparently constant entrapped air content (Figure 3.6) following the onset of dissolution may have been a consequence of preferential dissolution pathways. The breakthrough of a dissolution channel along only a partial section of a *TDR* probe could initially cause a decrease in measured entrapped air content followed by a period of little to no change as groundwater flow by-passed the remaining entrapped air surrounding the other portion(s) of the *TDR* probe. Then, with time, the finger widened or the main front reached the *TDR* probe, resulting in greater late-time trapped gas declines at that specific

TDR probe. Ultimately, dissolution channelling and/or fingering is caused by subtle differences in the hydraulic conductivity field due to micro-heterogeneities in the tank pack and subsequent spatial differences in entrapped air saturation (Farthing et al. 2012; and references therein). Such complex inter-phase mass transfer kinetics (beyond boundary layer effects) are expected to be common, and likely greater for real-world aquifer heterogeneity.

3.3.5 Detecting Entrapped Air and Monitoring Dissolution with P_{TDG}

Recall that immediately following the initiation of groundwater flow, P_{TDG} in the monitoring wells were equal to the local trapped gas pressure (P_G) or bubbling pressure (P_{G}), in comparison to the significantly lower and more variable head tank P_{TDG} values (Figure 3.4, Lane 1). Dissolution of entrapped air in the up-gradient quasi-saturated zone increased P_{TDG} in the groundwater from the source water level to equilibrium level, indicating the presence of entrapped air (Manning et al. 2003). In addition, the monitoring well P_{TDG} values fluctuated with slight changes in P_{atm} (total change <4.2 kPa or 42.7 cmH₂O) due to expansion-contraction of the entrapped air phase. For example, an increase in atmospheric pressure caused an equivalent rise in aquifer P_{TDG} as mass was transferred from the compressed gas phase into the aqueous phase, whereas a drop in P_{atm} caused a decrease in P_{TDG} because gas was stripped from the groundwater during the expansion of entrapped air. This response of the measured P_{TDG} to the fluctuating P_{G}^{*} (with variable P_{atm}) provides additional insight into the field conditions, indicating close proximity of a trapped gas phase to the measurement point. However, this characteristic response may not occur in groundwater systems lacking direct connection to P_{atm} , such as deep and/or confined aquifers.

Similar to the entrapped air content data (Figure 3.6), the continuous P_{TDG} readings remained relatively constant at P_{G}^{*} , before declining, first at the deeper monitoring depth and then at the more shallow depth (Figure 3.7; similar results were observed for all other wells in both lanes). Thus, P_{TDG} measurements less than P_{G}^{*} but still elevated above background levels can indicate the presence of entrapped air which is currently undergoing dissolution (Manning et al. 2003). The P_{TDG} readings within the monitoring wells eventually reached source water levels, as in the HTs (Figure 3.7, Lane 3), indicating that complete dissolution of the entrapped air had occurred (Klump et al. 2008). In addition, the observed onsets of P_{TDG} decreases and times to complete dissolution agreed reasonably well with initial reductions in entrapped air contents observed immediately upand down-gradient of each monitoring well (not directly shown, only illustrated with arrows in Figure 3.7). Furthermore, plotted centers of P_{TDG} declines showed linear progression of the dissolution front similar to that derived from the TDR data where rates of down-gradient advancement were consistently greater at increasing depths (Figure 3.5). However, the P_{TDG} data seem to overestimate front advancement compared to the TDR data at similar depths. This may be due to flow focusing by the well or unequal mixing of flows across the screened depth. Regardless, these data demonstrate that the P_{TDG} probes effectively captured the general passing of the dissolution front.



Figure 3.7: Total dissolved gas pressure (P_{TDG}) from monitoring well 1 (located 115 cm downgradient) at two depths, 60 cm (orange) and 130 cm (red); and the head tank (blue, average of both depths) from Lane 3, with the theoretical bubbling pressures (P_G) (grey = 60 cm, black = 130 cm). Arrows mark onset of dissolution captured from *TDR* probes at 45 cm (orange) and 135 cm (red) depths, located 70 cm (solid) and 155 cm (open) down-gradient of *HT*. Note, data gaps indicate periods of equipment maintenance and/or no flow conditions in the tank.

Unfortunately, the cause of noise in the P_{TDG} readings during continuous monitoring (Figure 3.7) is not known. It appeared mainly restricted to the passing of the dissolution front. Also, the magnitude of noise was significantly larger for the P_{TDG} probes positioned within the lower portion of the monitoring wells, where the screened interval and packer-isolated well volume was ~35% greater than the upper half. Possible causes include in-well convective circulation due to minor thermal gradients or variable bubble dissolution within the well or on the probe tubing itself. Determining the exact source of the P_{TDG} probe noise is an avenue for future research.

3.4 Conclusions

In summary, the pilot-scale tank experiment demonstrated the multidimensional nature of entrapped air dissolution with horizontal groundwater flow. Dissolution exhibited characteristic propagation along the groundwater flow path due to the constant inflow of under-saturated source water with respect to the local trapped gas pressure (P_G). In addition, the dissolution front at the water table advanced down-gradient 4.1 - 5.7x slower than at the deepest monitoring point, resulting in a wedge-shaped dissolution pattern. This suggests that gas trapped within the shallow groundwater zone will likely persist for significant periods of time, potentially on a timescale of years under horizontal flow, although recharge may shorten persistence of shallow entrapped air.

The observed depth-dependence of dissolution was influenced by two complementary mechanisms associated with entrapped air phase compression at greater water pressures (P_w). Increasing dissolved gas solubility was illustrated with P_{TDG} measurements, whereas decreasing air contents with depth, measured with *TDR*, were associated with a 12% increase in quasi-saturated hydraulic conductivity (K_{qs}). Calculations involving the measured dissolution front propagation velocity, considering the expected difference in flow with depth, quantified using K_{qs} results from a 1-D laboratory column suggest that this latter mechanism plays a more minor role compared to the enhanced gas solubility.

The results also indicate a more diffuse nature of the dissolution front compared to the sharp fronts reported in the literature from numerical models that only consider boundary-layer kinetics, indicating larger-scale mass transfer kinetics are involved even for this homogeneous sand tank. It may be revealed in future studies that the evolving hydraulic conductivity field associated with a complex entrapped air distribution will cause even more variable dissolution patterns in heterogeneous aquifers.

Furthermore, total dissolved gas pressure (P_{TDG}) probes were shown to be useful devices for the detection of entrapped air within the zone of the fluctuating groundwater table and for continuous monitoring of the dissolution process, despite the observed noise. Other means of monitoring entrapped air (e.g. neutron probe, evolving noble gas ratios, etc.) are more cumbersome and expensive. Given the significant impacts of a trapped gas phase on saturated hydraulic conductivity and the transport of volatile contaminants and dissolved gases, simple on-site screening for entrapped air can be useful for a wide variety of groundwater applications, including site characterizations and remediation techniques.

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APPENDIX 1

Supporting Information for Chapter 3:

Patterns of entrapped air dissolution in a two-dimensional pilot-

scale synthetic aquifer

Table A3.1: Overall bulk and flux (*q*)-scaled slopes of linear regressions from Figure 3.5 in addition to corresponding R^2 values. Regressions were forced through (0, 0).

	Lane 1			Lane 3		
Monitoring Point Depth Below Sand Surface	Slope of Linear Regressions			Slope of Linear Regressions		Correlation
	Bulk ^a	q-Scaled ^b	(n)	Bulk ^a	q-Scaled ^b	(n)
15 cm	5.8	8.3	-	5.3	7.9	-
45 cm	8.8	9.2	0.998	9.8	10.5	1.000
P _{TDG} 60 cm	13.7	14.2	0.997	14.1	14.7	-
75 cm	13.8	14.4	0.997	13.5	13.6	0.996
105 cm	15.6	15.1	1.000	16.5	16.1	0.990
P _{TDG} 130 cm	19.8	18.7	0.989	23.3	22.0	1.000
135 cm	18.4	17.3	0.979	20.1	19.1	0.987
165 cm	24.1	15.6	0.996	30.1	27.0	0.996

^a Overall bulk linear regressions were fit to data based on the total discharge rate out of each withdrawal well.

^b Flux (*q*)-scaled linear regressions were fit to the same data which was scaled to account for differences in K_r with depth.

- R² values were not reported since data series only had two points.

CHAPTER 4

A pilot-scale laboratory investigation of gas phase dynamics

within a groundwater hydrocarbon plume

4.1 Introduction

A variety of biogeochemical processes can produce dissolved gases in groundwater at sites with agricultural (e.g. Blicher-Mathiesen et al. 1998) or industrial (e.g. Amos et al. 2005) contamination. Substantial biogenic gas production is also known to occur in wetlands (e.g. Beckwith and Baird 2001; Strack et al. 2005). With respect to the natural remediation of dissolved hydrocarbons derived from petroleum- and/or ethanol- fuel spills, the microbial reactions with high gas-producing potential occur under anaerobic conditions. These reactions may include denitrification, reduction of metal oxides and sulphate, and methanogenesis. The occurrence and distribution of these reactions within contaminant plumes will depend on the bioavailability of electron acceptors, nutrients and organic substrates; in addition to the predominant redox conditions and microbial ecology (Wiedemeier et al. 1999).

Significant biogenic gas production associated with microbial hydrocarbon degradation can result in dissolved gas supersaturation and lead to the formation and/or expansion of an *in situ* gas phase, which have important implications for the fate and transport of groundwater contaminants. For instance, gas trapped within porous or fractured media can reduce the hydraulic conductivity and thus, limit groundwater flow (e.g. Soares et al. 1991; Dror et al. 2004; Amos and Mayer 2006a). It can also impede the replenishment of oxidants or nutrients (Fry et al. 1995; 1996; Donaldson et al. 1998), and the transport of contaminants (Cirpka and Kitanidis 2001), which control microbial biodegradation rates (Amos and Mayer 2006a). Gas phase expansion in the presence of a non-aqueous phase

liquid (NAPL) can mobilize the NAPL (Roy and Smith 2007; Mumford et al. 2009a), potentially leading to greater groundwater contamination. There is also the possibility of vertical mobilization of the gas phase (ebullition), which can affect contaminant vapour (e.g. NAPL compounds) and/or biogenic gas (e.g. methane, hydrogen sulphide, nitrogen gas) transport to soils and/or buildings, potentially posing significant explosion and asphyxiation risks (Spalding et al. 2011; Sihota et al. 2013; Ma et al. 2014). Moreover, the upward flux of biogenic gases via ebullition from wetlands and aquifers may contribute significantly to global greenhouse gas emissions (Rosenberry et al. 2003; Amos and Mayer 2006b).

Several groundwater studies have examined biogenic gas production and associated trapped gas dynamics using small-scale laboratory systems (≤ 100 cm in length) under stagnant (no-flow) conditions. For instance, Istok et al. (2007) measured increases in trapped gas saturations during denitrification in a 2-D glass flow cell packed with crushed limestone using a gamma imaging system. The temporal images revealed that the expanding gas phase coalesced into larger ganglia before migrating upward through disconnected gas-filled channels and out the top of the cell. As a result, the maximum gas saturations measured over experimental duration (14 days) did not exceed 23.0% of the pore volume and had no significant impacts on sediment pack hydraulic conductivity based on manometer readings. Furthermore, Amos and Mayer (2006b) quantified ebullition from a 1-D sand column over 56 days using dissolved gas analysis and numerical modeling. Results demonstrated that 36% of the methane and 19% of

the carbon dioxide produced from an organic layer at the bottom of the column was rapidly transported to the top as a result of gas phase mobilization.

Degassing due to biogenic gas generation has also been inferred at hydrocarbon-impacted field sites using mass balance calculations (e.g. Baedecker et al. 1993), measured depletions in non-reactive tracer gases, such as argon and nitrogen (e.g. Revesz et al. 1995; Amos et al. 2005); and from surficial soil vapour measurements above hydrocarbon plumes (e.g. Sihota et al. 2013). In these field studies however, individual gas phase processes and their relative significance could not be distinguished. A numerical model (Amos and Mayer 2006a; 2006b), though largely empirically-based, has also been employed for both lab and field based studies to better elucidate the effects of such gas phase behaviours on groundwater flow and aqueous geochemistry.

The primary objective of this study was to examine, at a fieldrepresentative scale, trapped gas changes within a groundwater plume of dissolved hydrocarbons undergoing anaerobic biodegradation. Of particular interest was the pattern of biogenic gas production and associated gas phase dynamics, including the potential for trapped gas mobilization; which have not been fully investigated, especially over larger spatial and temporal scales. The experiment was implemented in a highly-instrumented, two-dimensional (175 cm high × 525 cm long), pilot-scale, laboratory tank. Experimental conditions mimicked a homogeneous, unconfined sand aquifer with horizontal groundwater flow and a residual gas phase following a water table fluctuation. *In situ* trapped gas saturations were directly measured near-continuously with Time Domain

Reflectometry (*TDR*) probes while dissolved gas and aqueous geochemical analyses of the groundwater were used to monitor the biodegradation processes. Dissolved hydrocarbons (ethanol, methyl *tert*-butyl ether (MTBE) and toluene) were continuously injected into the synthetic aquifer over 330 days. Ethanol was added as the primary organic substrate to promote and sustain significant biogenic gas production, whereas MTBE and toluene were added at lower concentrations, as representative petroleum tracers with a range of volatilities and recalcitrance to degradation.

4.1.1 Relevant Theory on Gas Phase Dynamics

In situ trapped gas formation (exsolution) is expected to occur when the total dissolved gas pressure (P_{TDG}), which is the sum of the partial pressures that would be in equilibrium with the concentrations of dissolved gases in the bulk aqueous phase, exceeds the bubbling pressure (P_{G}^{*}); that is, when $P_{TDG} > P_{G}^{*}$. Note that in the presence of pre-existing seed bubbles (or nucleation sites),

$$\boldsymbol{P}_{\boldsymbol{G}}^{*} = \boldsymbol{P}_{\boldsymbol{w}} + \boldsymbol{P}_{\boldsymbol{c}} \tag{1}$$

where P_w is the prevailing water pressure and P_c is the capillary pressure (refer to Equation 4 for more details) (Li and Yortsos 1995; Jones et al. 1999). Thus, gas exsolution will preferentially occur at shallower depths and in coarser materials, all else being equal.

Following trapped gas formation and/or entrapment, mass exchange across the gas-water interface will direct the system towards equilibrium between the groundwater and the gas phase. At equilibrium, for a given gas *i*, its partial

pressure in the gas phase (p_{gi}) is related to its dissolved concentration (C_{gi}), as described by Henry's Law:

$$K_{Hi}(T,S) = \frac{p_{gi}}{R \cdot T \cdot C_{gi}}$$
(2)

where *R* is the universal gas constant, *T* is the absolute temperature, and K_{Hi} is the gas' dimensionless Henry's Law proportionality coefficient, which is dependent on temperature (*T*) and salinity (*S*), but is otherwise constant. It is apparent from Equation 2 that an increase in C_{gi} will induce mass transfer from the groundwater into the gas phase, increasing p_{gi} , or vice versa.

Equilibrium partitioning between the phases is more complicated when multiple gases are involved because equilibrium must be established for each individual gas species. Thus, mass transfer of different gases may occur in opposite directions according to Equation 2 and each gas' specific K_{Hi} and C_{gi} . However, these will be coupled through Dalton's Law, which states that the total pressure of the trapped gas phase (P_G) is equal to the sum of all the partial pressures of the gases present, that is,

$$\boldsymbol{P}_{G} = \sum \boldsymbol{p}_{gi} \tag{3}$$

Inter-phase mass transfer of all the gas species will also be influenced by changes to P_{G} , which can be affected by a number of external forces, according to

$$\boldsymbol{P}_{G} = \boldsymbol{P}_{w} + \boldsymbol{P}_{c} = \left(\boldsymbol{P}_{atm} + \boldsymbol{\rho} \cdot \boldsymbol{g} \cdot \boldsymbol{h}\right) + \left(\boldsymbol{\sigma}\left(\frac{1}{r_{1}} + \frac{1}{r_{2}}\right)\right)$$
(4)

where P_w is a function of the barometric pressure (P_{atm}), and the density of water (ρ), the acceleration due to gravity (g), and the hydraulic head (h; equal to the depth below the water table under hydrostatic conditions); and P_c is related to the interfacial tension of water (σ) and the curvature of gas-water interfaces (where r_1 and r_2 represent the principal radii of curvature of the trapped gas ganglia, which have a simplified ellipsoid shape) following the Young-Laplace Equation. For simplicity, P_c is commonly ignored or assumed to be negligible for coarse-grained aquifers, given the expected radii of the gas-water interfaces (Manning et al. 2003; Klump et al. 2007, 2008). But neglecting P_c may underestimate the P_{TDG} required to induce exsolution, forming a gas phase; and also potentially overestimate gas phase expansion (Amos and Mayer 2006a).

From the above relationships, it is clear that where $P_{TDG} < P_G$, the trapped gas phase will dissipate into the aqueous phase because the groundwater is under-saturated with dissolved gases compared to the local trapped gas pressure (Holocher et al. 2003). In addition, the driving force for dissolution will increase at greater depths below the water table and in finer materials, given the influence of P_w and P_c on P_G (Equation 4, Holocher et al. 2003; Klump et al. 2008; McLeod et al. 2015); and where dissolved gases are being consumed by biogeochemical reactions, such as aerobic degradation (with concurrent dissociation of produced carbon dioxide to ionic species; Ryan et al. 2000).

Alternatively, where $P_{TDG} > P_G$, the trapped gas phase will expand due to dissolved gas supersaturation which drives mass from the groundwater into the gas phase. This growth condition is expected to dominant where anaerobic

respiration occurs given that these reactions result in a net generation of dissolved gases (Table 4.1; Ryan et al. 2000).

Table 4.1: Typical redox reactions that occur in groundwater, provided in the order of increasingly reducing conditions with gaseous compounds identified in bold (Top) (modified from Ryan et al. 2000). Henry's Law Constants of common groundwater gases at 25°C, listed in the order of increasing aqueous solubility (Bottom) (Sander 1999).

Redox Reaction	Equation		
Aerobic Oxidation	$CH_2O^a + O_2 \rightarrow CO_2 + H_2O$		
Denitrification	$5CH_2O + 4NO_3^- + 4H^+ \longrightarrow 2N_2 + 5CO_2 + 7H_2O$		
Iron Reduction ^b	$CH_2O + 4Fe(OH)_3 + 8H^+ \longrightarrow 4Fe^{+2} + CO_2 + 11H_2O$		
Sulfate Reduction	$2CH_2O + SO_4^{-2} \longrightarrow H_2S + 2CO_2 + 2H^+$		
Methanogenesis	$2CH_2O \longrightarrow CH_4 + CO_2$		
Gas Species	Henry's Law Constant at 25ºC $\left(rac{mol}{L\cdot kPa} ight)$		
N ₂	6.22 × 10 ⁻⁶		
H ₂	7.70 × 10 ⁻⁶		
O ₂	1.25 × 10 ⁻⁵		
CH ₄	1.37 × 10 ⁻⁵		
CO ₂	3.36 × 10 ⁻⁴		
H ₂ S	9.66 × 10 ⁻⁴		

^a To simplify, CH₂O was used to represent organic matter; but other organic compounds, such as petroleum hydrocarbons, can also be oxidized.

^b Can also be manganese reduction with a similar trend in gas generation.

However, the resultant dissolved gas supersaturation (or likelihood of growth) will depend on the type of gases (i.e., their aqueous solubilities, see Table 4.1) and the relative abundances in which they are produced (i.e., aqueous concentrations) based on Equation 2. Previous studies have also demonstrated that continued mass transfer into the gas phase can result in its fragmentation and vertical mobilization, as buoyancy forces surpass the local capillary forces that trap the gas phase (Tsimpanogiannis and Yortsos 2004; Roy and Smith 2007).

Finally, within a flow system, mass transfer between groundwater and trapped gas at one location can influence gas phase dynamics down-gradient. For instance, equilibration between the phases regulates groundwater P_{TDG} at P_G and potentially eliminates the chemical gradient for mass transfer at down-gradient locations under strict horizontal flow conditions. Thus, gas-water interactions in the up-gradient quasi-saturated zone will tend to inhibit trapped gas dissolution (Klump et al. 2008; McLeod et al. 2015) or growth, including the potential for gas phase mobilization (Mumford et al. 2009a), at down-gradient locations if dissolved gas production is negligible there.

4.2 Methods

4.2.1 Experimental Set-up

The pilot-scale synthetic aquifer was assembled using approximately 36.2 metric tonnes of BARCO M49 medium silica sand (Opta Minerals, Waterdown, Ontario, Canada) in a stainless steel tank (600 cm long × 240 cm wide × 180 cm

deep; Figures 4.1 and 2.3) located at the Canada Centre for Inland Waters in Burlington, Ontario, Canada. The overall average porosity (*n*) of the packed tank was 37.6%. The tank was divided lengthwise into three separate test lanes, each 80 cm wide with an open reservoir or head tank (*HT*, 80 cm wide × 75 cm long) located at one end and separated from the aquifer (i.e., sand-packed section) by a steel perforated plate affixed with a non-woven polypropylene geotextile (Nilex, Toronto, Ontario, Canada). Only one lane was used in this study (Lane 3, Figure 2.3A) which was packed to be homogeneous. Further details on the sand properties and the packing procedures are provided in Chapter 2.

Prior to this study, the tank was refilled after drainage using water inoculated with a microbial community from a field site with previous hydrocarbon contamination (see Chapter 2). The final position of the water table was established ~ 5 cm below the sand surface, thus saturating (except for trapped gas) the entire aquifer thickness, in part by capillary rise. A dissolution experiment was then conducted over the next 12 months (16.5 pore volumes of synthetic groundwater passed, Chapter 3). Consequently, the trapped gas at nearly half the *TDR* locations underwent complete dissolution, producing a wedge-shaped zone of fully water-saturated conditions up-gradient of a region of persisting quasi-saturation; representing the initial conditions for this study.

The synthetic groundwater used in the tank was composed of dechlorinated tap water amended with nutrients, that is, 310 μ M and 72 μ M of NH₄NO₃ and K₂HPO₄, respectively. Nutrients were increased by a factor of 2 several months into the experiment to help boost denitrification. The source

water was gravity fed into the head tank, which was equipped with an industrial brass float valve to maintain the up-gradient constant head boundary condition. Groundwater flow was generated by pumping with a peristaltic pump from one fully screened 4-inch PVC withdrawal well centered at the end of the lane, 520 cm from the *HT* (Figure 4.1 and 2.3). A constant withdrawal well rate was applied to maintain an average linear groundwater velocity of 20.7 ± 1.8 cm/day, analogous to natural fast flowing homogenous sand aquifer. At the selected velocity, a pore volume (*PV*), defined here as the water volume within the sand-filled section of a lane (i.e., 1 PV = 2760 L), was passed every 25.4 days, approximately.

Three 4-inch PVC injection wells (*IWs*) were installed as a fence across the lane 30 cm down-gradient of the *HT* (Figure 4.1). These were fully-screened and well mixed by a peristaltic pump that circulated water from the bottom to the top at a rate 3.3x faster than the total bulk discharge rate out of the lane. An aqueous mixture of ethanol (Commercial Alcohols), MTBE (Sigma Aldrich) and toluene (Fisher Chemical) was injected just below the water surface in each injection well at a constant rate of 2.3 ± 0.3 mL/min using a low flow, precision peristaltic pump. This acted as a uniform and continuous source for the dissolved hydrocarbon plume. The hydrocarbon stock mixture was manually prepared in 23.0 L glass bottles every second day using the synthetic groundwater and high purity (> 99%) chemical grades of the selected hydrocarbons. The dissolved hydrocarbon contamination was initially added to the *IWs* by means of a stepwise increase, which was achieved by turning on the hydrocarbon delivery

system (via low flow peristaltic pump) and immediately spiking each injection well with a single concentrated dose of hydrocarbons (and inorganic tracer, KBr). Note, the total ethanol loading (maximum concentrations) in both the stock solution and *IWs* was always less than 0.5% by weight, thus avoiding any changes in the viscosity, density or interfacial tension of the aqueous phase (Sciortino and Leij 2012).



Figure 4.1: The cross-sectional profile (A) and plan view (B) of the experimental design for the test lane used in the pilot-scale tank. The dotted line represents the sand surface, whereas the solid blue roughly represents the position of the water table. Ambient groundwater flow occurred from left to right; from head tank (*HT*) to withdrawal well, where hatched sections correspond to screened intervals of wells. Three injection wells (*IWs*, 30 cm from *HT*) were installed as a fence to introduce an aqueous hydrocarbon mixture into the synthetic aquifer. Passive gas samplers (*PGS*), dissolved oxygen (*DO*) and total dissolved gas pressure (*P_{TDG}*) probes (red stars) hung in the *HT* (0 cm) and three monitoring wells (*MW1*, *MW2*, and *MW3*), located 115, 250 and 375 cm down-gradient, at two vertical positions (60 and 130 cm) separated by packers. *TDR* probes and groundwater samplers (*GWS*) were distributed at 6 vertical depths below sand surface (15, 45, 75, 105, 135 and 165 cm) along five *in situ* instrument arrays (in green) located 70, 155, 205, 320, and 445 cm down-gradient of *HT*.

A full set of sampling was performed prior to hydrocarbon injection (July 11, 2012; t = -37 days, PV = -1.4) to characterize the initial background conditions. The current experiment was then initiated with the onset of hydrocarbon injection on August 17, 2012 (t = 0 days, PV = 0.0) where dissolved hydrocarbon contamination was added over 12.9 pore volumes (328 days), followed by an additional 1.7 PV of groundwater to remove any remaining contamination (t = 330 - 372 days, end date August 24, 2013, total number of PV passed = 14.6). Monthly groundwater sampling commenced after initial hydrocarbon break-through on September 28, 2012 (t = 42 days, PV = 1.7), until June 13, 2013 (t = 300 days, PV = 11.8) except during the Transition Period (see Section 4.3.1), which was sampled bi-monthly over December 2012 to January 2013 (t = 93 - 164 days, PV = 3.7 - 6.5). All data has been plotted relative to time, that is, the number of days elapsed since the initial hydrocarbon release (t = 0) days), because the discharge rate out of the lane was essentially constant. All effluent was treated to remove persisting hydrocarbon contamination before being released to a municipal drain (refer to Chapter 2 for treatment system details).

4.2.2 Instrumentation

Thirty 30-cm long, three-pronged stainless steel Time Domain Reflectometry (*TDR*) probes (Campbell Scientific, Edmonton, Alberta, Canada) were embedded horizontally in the sand during packing (Figure 2.2). These probes were distributed at six different depths (15, 45, 75, 105, 135 and 165 cm)

below the sand surface and along five instrument arrays or transects located 70, 155, 205, 320 and 445 cm from the HT (0 cm) (Figure 4.1). *TDR* waveforms from each probe were collected at 2 - 6 h intervals and interpreted with the empirical relationship of Topp et al. (1980) to compute volumetric moisture contents. Gas contents (% of bulk volume) were calculated by subtracting measured volumetric water contents at a given location from a porosity value (*n* or n_e ; refer to Chapter 2 for full description of trapped gas calculations and details regarding the *TDR* data acquisition system).

Each *TDR* probe was coupled with a groundwater sampler consisting of a 3-inch stainless steel, 40- μ m porous cup (Chand Eisenmann Metallurgical, Burlington, Connecticut, USA) connected to stainless steel tubing (Figure 2.5A). Designated HDPE 30 mL syringes were used to purge the lines and collect representative groundwater samples, analyzed for aqueous hydrocarbon, nutrient and major ion concentrations. Details regarding the treatments and storage conditions of the collected samples; in addition to the types and associated detection limits of the analytical quantification methods used are included in Table 4.2 (refer to Chapter 2 for all analytical procedures). Collected inorganic geochemical data was used to estimate total dissolved inorganic carbon (*DIC*) concentrations as the shortfall in anionic charges following charge balance calculations based on the principle of electroneutrality. Thus, *DIC* concentrations were used for qualitative purposes only due to the high level of uncertainty inherently associated with charge balance calculations.

Table 4.2: Summary of groundwater sa	ample details including	container type,	sample treatment,
storage, analytical quantification method	d and associated detect	ion limits.	

Analyte	Container	Sample Treatments	Storage Conditions	Analytical Methods	Method Detection Limits (μM)
Hydrocarbons	20 mL, glass vial with mininert valve	No headspace, preserved with 0.1 g of sodium bisulphate	Refrigerated at 4°C for ~14 days	P&T GC-MS	Ethanol (1.10), MTBE (0.10) & Toluene (0.10)
Major Anions	30 mL, HDPE bottle	Filtered through 0.20 µm sterile syringe filter	Refrigerated at 4°C for ~ 30 days	IC	Br ⁻ (0.25), Cl ⁻ (0.30), F ⁻ (0.20), NO ₂ ⁻ (0.20), NO ₃ ⁻ (1.10), PO4 ⁻³ (0.20) & SO ₄ ⁻² (0.50)
Major Cations	125 mL, HDPE bottle	Filtered through 0.20 µm sterile syringe filter and acidified to pH<2 with 10% nitric acid (HNO ₃)	Indefinite shelf life	ICP-OES	Al ⁺³ (1.20), Ca ⁺² (0.50), Fe ⁺² (0.40), K ⁺¹ (3.00), Mg ⁺² (0.25), Mn ⁺² (0.50) & Na ⁺¹ (0.20)
Ammonium	30 mL, HDPE bottle	No headspace , filtered through 0.20 µm sterile syringe filter and acidified to 5 <ph<6 10%<br="" with="">hydrochloric acid (HCI)</ph<6>	Frozen, indefinite shelf life	UV/Vis-S	(1.50)

Three 4-inch PVC monitoring wells (*MW*) screened over two depth intervals were located along the flow path at 115, 250, and 375 cm from the *HT* (Figure 4.1 and 2.6). These wells hosted two sets of passive gas samplers (*PGS*), luminescent dissolved oxygen (*DO*) sensors and total dissolved gas pressure (P_{TDG}) probes, at two depths approximately 60 cm (upper) and 130 cm (lower) below the sand surface (Figure 2.6). Upper and lower halves of the monitoring wells were isolated by thin custom rubber baffles to prevent vertical flow in the wells. The same configuration of monitoring well equipment was also placed in the open *HT* to monitor the source water. The *PGS* were assembled following the procedures described by Spalding and Watson (2006) prior to being secured to the *DO* probes for installation into the monitoring wells (refer to chapter 2 for the details regarding passive gas sampler materials). All monitoring well equipment was removed every 30 days for probe maintenance.

The DO sensors (HACH Company, Loveland, Colorado, USA) recorded dissolved oxygen concentrations (mg/L) and groundwater temperature (°C) every 30 minutes and the P_{TDG} probes (Point Four Systems, Coquitlam, British Columbia, Canada) recorded hourly pressure readings (kPa). The PGS were used to collect gas in equilibrium with groundwater for measurement of dissolved gas composition (i.e., the abundance or percent of N₂, O₂, CO₂, CH₄ and H₂ by volume) roughly every 60 days. Duplicate PGS measurements were quantified by gas chromatography where detection limits for each gas were 0.50, 0.50, 0.05, 0.05 and 0.10% by volume, respectively (refer to Chapter 2 for analytical procedures and corresponding calibration statistics, Table 2.3). Percent of the total dissolved gas composition for a given gas could be converted to a partial pressure and/or aqueous concentration using the corresponding P_{TDG} reading (i.e., the daily average prior to PGS collection) and a temperature specific Henry's Law constant which accounted for differences in groundwater temperature ($25 \pm 8^{\circ}$ C).

4.3 Results and Discussion

4.3.1 Input Conditions

The source water geochemistry mimicked anaerobic groundwater within a sand aquifer with high nitrate loadings. Anaerobic conditions were maintained in the source water throughout the experiment, apparently via NH_4NO_3 nutrient amendments that sustained nitrogen fixation by microbial activity, that is, the oxidation of NH_4^+ to NO_3^- using dissolved oxygen (Equation 1, Table A4.1; also

refer to Chapter 2). In fact, O_2 concentrations in the *HT* were typically less than 15 μ M (0.5 mg/L; not shown). It is not uncommon for groundwater systems to become anoxic via aerobic degradation following petroleum hydrocarbon contamination due to the lack of rapid O_2 replenishment. The average input electron acceptor pool, measured within the head tank, was approximately 510 and 310 μ M of nitrate and sulphate, respectively; with the nitrate concentrations increased to 740 μ M on day 93.

The original target input hydrocarbon concentrations within the injection wells (*IWs*) for ethanol, MTBE and toluene were 22000, 550 and 550 μ M, respectively (gray dashed line, only ethanol shown in Figure 4.2). These concentrations were calculated using the stock concentrations (i.e., the weight of hydrocarbon added to the 20 L stock solution), the hydrocarbon injection rate and the bulk discharge rate from the lane, scaled by the ratio of the cross-sectional areas of the injection well fence to the aquifer (0.35). However, the actual measured hydrocarbon concentrations within the *IWs* during the experiment were 1.7 to 2.5 times higher (e.g. on average 55600, 1400 and 940 μ M, for ethanol, MTBE and toluene, respectively) and were variable in time (green symbols and line, Figure 4.2). The observed accumulation of hydrocarbon mass within the *IWs* indicates reduced well efficiency characteristic of clogging of the well screens and/or the surrounding sand pack due to biofilm growth and/or microbial gas production (see Baveye et al. 1998; and references therein). These data (Figure 4.2) suggest that major clogging occurred within the first 10 days as measured concentrations deviated from expected during the introductory hydrocarbon spike

initiating this experiment. Likewise, it appeared that all three *IWs* were similarly affected since the hydrocarbon concentrations and their trends through time within each well were comparable (not shown directly; note standard deviation in Figure 4.2).



Figure 4.2: Average ethanol concentration measured within the injection wells (green symbols and line), in comparison to its concentration in the hydrocarbon stock solution (black dashed line) and its expected concentration in the injection wells in the absence of bioclogging (gray dashed line). Symbol error bars represent one standard deviation. The experiment was divided into two Stages and a Transition Period (shaded grey zone) due to changes in the hydrocarbon source as a result of the bioclogging in or near the injection wells.

There are several additional lines of evidence that support the bioclogging hypothesis and that suggest the depths where clogging impeded input from the *IWs* changed dramatically over time. For example, during early times (Stage 1; 10 - 92 days), the dissolved hydrocarbon source was shallow gradually

decreasing at depth (Figure 4.3A, t = 67 - 89 days). Whereas, during later times (Stage 2; 165 - 328 days), the hydrocarbon source was predominantly deep (Figure 4.3A, t = 187 - 300 days), mainly affecting the 105 – 165 cm monitoring depths. A similar pattern is apparent in the break-through of several inorganic tracer (KBr) test pulses (Figure S4.1, refer to Chapter 2 for procedures). These show that during early times (Stage 1, Figure S4.1B), the injection well efficiencies were much reduced in the lower portion of aquifer, observed as an increasingly dampened tracer pulse response at depth, which was opposite to the tracer response prior to initiation of the experiment (Figure S4.1A). Meanwhile, later during the experiment (Stage 2; Figure S4.1C), little to no tracer pulse response was observed shallowly and the deep tracer response was more pronounced than at the early times. These changes demonstrate that the predominant depth of *IW* clogging reversed between these two time periods.

It is unclear why the bioclogging of the injection wells started preferentially at deeper depths, though the downward circulation in the *IWs* may have helped transport biomass in that direction. It is also unknown why the clogging then shifted so significantly between these two stages (i.e., during the Transition Period, t = 93 - 164 days). However, nutrient additions (e.g. increased by a factor of 2 in step-wise manner to boost denitrification on day 93) and an accidental release of hydrocarbon waste to the *HT* on day 103 during tank maintenance may have contributed. Bioclogging is not an uncommon phenomenon, occurring in or near injection wells, infiltration or artificial recharge galleries, and permeable reactive barriers used in groundwater bioremediation strategies that promote microbial activity (see Seki et al. 2006; Clement 2011), not unlike the conditions in this study.

As described above, the injection well bioclogging led to changes in the spatial distribution of hydrocarbon input to the tank during the experiment. This was not the original design. However, regardless of input, there is ample evidence of biodegradation occurring in the tank, resulting in substantial changes to the gas phase, which will be discussed in detail in the following sections. In addition, these conditions are still representative of real contaminated sites, where spatially- and temporally- variable contaminant plume configurations may occur due to heterogeneous source zone morphologies, water table fluctuations, seasonal variations in recharge, changing groundwater flow directions, and remediation activities. Overall, given the strong influence of bioclogging on the input of hydrocarbons during this experiment, all results were presented and discussed in reference to two Stages (Stage 1 – early; Stage 2 – late), as described above, with a Transition Period between them.

Finally, regardless of the bioclogging issues, the input ethanol concentrations were 11.4 to 76.1 times lower than the reported toxicity levels for microbes (i.e., concentrations > 6 - 40% by weight, Hunt et al. 1997; Nelson et al. 2010). Also, they were consistent with groundwater concentrations measured following large-scale, accidental releases of denatured ethanol (95% ethanol, 5% gasoline) (Spalding et al. 2011) but were higher than groundwater concentrations typical of petroleum- and/or gasohol (15% ethanol, 85% gasoline)- fuel plumes. Despite these higher concentrations, it is expected that the observed gas

behaviors will be generally applicable to hydrocarbon plumes undergoing anaerobic biodegradation.

4.3.2 General Patterns of Microbial Hydrocarbon Degradation

It should be noted that the intent of this section was to establish the occurrence and distribution of biodegradation in the synthetic aquifer during experimental duration, including the types of microbial-mediated reactions utilized with broad implications for trapped gases. A more in-depth look at some of these biogeochemical patterns in relation to gas phase processes will follow in Section 4.3.4. But overall, the nature of microbial hydrocarbon degradation observed could benefit from further biogeochemical discussion, quantitative interpretation and/or numerical model simulation (e.g. Amos and Mayer 2006a); however, this was beyond the scope of the current study.

4.3.2.1 Evidence of Hydrocarbon Biodegradation

The spatial plots of ethanol concentrations within the tank are strongly suggestive of a contaminant plume undergoing biodegradation (Figure 4.3A), with declines more than an order of magnitude from the heart of the plume to the end of the tank. A similar pattern was observed for MTBE and toluene (not shown). Within Stage 1 and Stage 2, the hydrocarbon plume appears to be at a steady-state, eliminating sorption as a dominant process for the concentration pattern. Physical mixing along the flow path, predominantly lateral dispersion, however, could not be ruled out as a cause of the declining concentrations.







Figure 4.3: Spatial distributions of ethanol (A), dissolved inorganic carbon (DIC, B), nitrate (C), nitrite (D), ammonium (E), iron (II) (F), sulphate (G) and the monthly rates of change in trapped gas saturations (ΔS_G / PV, H) throughout the test lane over time for each sampling event (t = -37 to 300 days). For analytes A to G, the shade of gray is proportion to its aqueous concentration, that is, darker grays represent higher concentrations and lighter grays represent lower concentrations. However, the contouring intervals may be different for each analyte: in addition regular contours are represented as solid lines, whereas extra contours are included as dashed lines (refer to colour scales above). For H, positive rates (vellows) indicate increasing gas saturations; while negative rates (blues) suggest decreasing saturations. Open diamond symbols mark the locations of the TDR probes and groundwater samplers. All data was interpolated with the linear triangulation grid method (honors data exactly) in Surfer Software (Golden Software Inc., Golden, Colorado, USA).

This is because the *IWs* do not span the full width of the test lane (injection well fence width / lane width ratio = 0.35; though convergent flow into the wells will increase this value somewhat), resulting in three out-flowing plumes across the width of the tank. This was further exacerbated by the bioclogging issue, which means reduced flow through the *IWs*, potentially even divergent of flow around the wells, which would effectively reduce the above ratio to less than 0.35. Unfortunately, the true value of this ratio and thus, an estimate of the effect of dispersion could not be determined.

Although, dispersion contributed to concentration decreases, there was also ample other evidence of hydrocarbon biodegradation in the tank, including:

- i) Increases in dissolved inorganic carbon concentrations (Figure 4.3B), which is associated with microbial production of CO₂.
- **ii)** Loss of nitrate (Figure 4.3C), which is suggestive of denitrification.
- iii) Increases in dissolved iron concentrations (Figure 4.3F), which may imply iron (III) reduction.
- iv) Loss of sulphate (Figure 4.3G), which is indicative of sulphate reduction.
- v) Generation of methane (Figure 4.5), which is a product of methanogenesis.
- vi) Production of hydrogen gas (Figure 4.5) likely derived from fermentation processes.

All of the above processes are known to occur with the biological oxidation of hydrocarbons (see Table 4.1, but for vi), which are discussed in the following sections. However, the spatial patterns of DIC concentrations is especially informative because CO_2 production, which can induce significant increases in DIC following chemical speciation (Hunkeler et al. 1998; 1999; Illman and

Alvarez 2009), is an end-product of all of the common biodegradation processes regardless of electron acceptor (Table 4.1). Hence, DIC values elevated above background (i.e., < 10 mM, Figure 4.3B, t = -37 days), indicate that some degree of biodegradation has occurred. This was observed throughout the experimental duration (e.g. Figure 4.3B, t > 42 days). Spatially, DIC values increased along the groundwater flow path (e.g. Figure 4.3B, t = 67 days) indicating hydrocarbon biodegradation throughout the tank and consistent with continuously declining ethanol concentrations (Figure 4.3A). Furthermore, the greatest down-gradient DIC concentrations (which varied in time due to bioclogging); for example, at shallow depths during Stage 1, and then deeper depths for Stage 2 (e.g. compare 67 to 187 days in Figure 4.3A and B). Further details on the other microbially-mediated processes (ii – vi) will be discussed in Sub-Section 4.3.2.2.

While it is apparent that biodegradation was occurring in the tank, the above lines of evidence do not identify which of the hydrocarbons were degrading. Consider the depth-averaged hydrocarbon concentrations (all 3 compounds, note the log scale) at each of the five monitoring arrays (distances of 70, 155, 205, 320 and 445 cm from the *HT*), over the duration of the experiment, as shown in Figure 4.4. The range of hydrocarbon concentrations in the *IWs* is indicated (green shaded area in Figure 4.4), with concentrations in the tank substantially below this, and generally declining at any given time from the first transect (70 cm) to further transects down-gradient. Also included was the maximum reduction in concentrations due to the complete mixing of the input

hydrocarbons across the aquifer's cross-sectional area (i.e., perpendicular to the average flow). This fully-mixed concentration (black dotted line in Figure 4.4) was calculated from the hydrocarbon input rate to the three *IWs* and the bulk discharge rate out of the lane. This is likely an overestimate considering the reduced flow out to bottom and top portions of the injection wells during Stages 1 and 2, respectively; however, reductions in the concentrations below this value is clear proof of mass loss (considering quasi steady-state conditions) and a strong indicator of microbial hydrocarbon degradation.

It is apparent from Figure 4.4, that ethanol was substantially biodegraded since its concentrations at all transects, except the first (70 cm), were below the fully-mixed concentration threshold. Toluene also showed trends suggestive of microbial degradation with concentrations past the first transect falling below the mixing threshold as well, though the observed declines were much smaller in comparison to ethanol. Biodegradation of MTBE however, was much less certain since its concentrations at all monitoring locations were near or above the mixing threshold for the majority of the experiment. This is consistent with reports of high recalcitrance of MTBE to microbial degradation in the field (refer to Fayolle et al. 2001; Schmidt et al. 2004); however, since complete mixing across the full height of the plume was not expected, it is suspected some biodegradation of MTBE might have occurred. Overall, these results, that is, patterns of hydrocarbon mass loss coupled with evidence of biodegradation reactions (e.g. DIC gains) and concentration reductions beyond that expected by mixing processes, corroborate the occurrence of biodegradation within the synthetic aguifer.

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Figure 4.4: Changes in the depth-averaged hydrocarbon concentrations (μ M; log scale) for each *in situ* array over experimental duration. Instrument arrays are located 70 (light blue circles), 155 (dark green triangles), 205 (blue squares), 320 (light green diamonds) and 445 cm (navy blue circles) down-gradient of the head tank (*HT*). For reference, the input concentration ranges measured within the injection wells (*IW* Range; shaded green section) and the estimated plume concentrations following the complete mixing of injection well input over the entire cross-sectional area of aquifer (Fully Mixed; black dashed line), are also included.

4.3.2.2 Degradation Pathways and Resultant Changes in Geochemistry

Major changes in the distribution of inorganic solutes, such as NO_3^{-} , Mn^{+2} , Fe⁺², SO₄⁻² (e.g. Figure 4.3C to G), and dissolved gas composition determined from the passive gas samplers (PGS) (Figure 4.5), document the series of microbial-mediated processes involved with hydrocarbon biodegradation. For example, the large stock of NO_3^- added to the source water was generally completely consumed within the aguifer (Figure 4.3C) except for some minor breakthrough at very shallow depths (\leq 15 cm below the sand surface) near the end of the experiment (t > 213 days). Nitrate attenuation, along with limited production of NO_2^{-1} (Figure 4.3D), an intermediate reaction product, suggests that the hydrocarbons were degraded via heterotrophic denitrification, resulting in N_2 gas production; though this is not apparent in the dissolved gas composition data (Figure 4.5) since N₂ was already abundant in the source water. Other processes that utilize NO₃⁻ and hydrocarbons, such as ammonification (Equation 4, Table A4.1; also refer to Rivett et al. 2008), also could have occurred and reduced the extent of heterotrophic denitrification. Possible evidence of ammonification was given by increases in NH_4^+ (i.e., above 150 μ M, HT concentration during Stage 2) within the synthetic aquifer, which superimpose over the hydrocarbon source (e.g. Figure 4.3E, t = 264 days).

Other degradation reactions included manganese (IV) and iron (III) reduction, with trace oxide minerals in the chemical composition of the M49 sand suspected as the source of these metals (refer to Table 2.1). Initial dissolved Mn^{+2} and Fe⁺² concentrations were below the detection limits in the source water

and throughout the tank prior to the experiment, but these subsequently increased within the synthetic aquifer. Manganese (IV) reduction was likely very minor, with maximum Mn⁺² concentrations less than 10.0 μ M, and as a result, it will not be discussed further (Mn⁺² not shown in Figure 4.3). Whereas, dissolved iron generation was substantial with concentrations ranging up to 590 μ M (Figure 4.3F). The resultant Fe⁺² plume slowly propagated down-gradient over time, leaving behind an ever increasing 'iron-free' zone (in this case, Fe⁺² concentrations \leq 50 μ M, approximately). This suggests that the degree of iron (III) reduction was diminishing over time as the fraction of bioavailable iron in the mineral phase of the sand was depleted (e.g. Lovely et al. 1989).

Sulphate reduction coupled with the biological oxidation of hydrocarbons was also suspected given the decreases in SO₄⁻² relative to its background concentration in the source water (Figure 4.3G). In general, sulphate distributions within the hydrocarbon plume showed similar patterns to nitrate, largely decreasing slightly further down-gradient of the *IWs*. Its gaseous end-product, H₂S (dominant species at pH \leq 6.5), was not monitored (not included in Figure 4.5), though some H₂S production was noted via its characteristic odour during sampling events. Given that H₂S is highly reactive with divalent metals, it is possible that dissolved Fe⁺² and H₂S were scavenged out of solution by the precipitation of iron sulphide minerals (Chapelle and Lovely 1992), where zones of iron (III) and sulphate reduction overlapped in the synthetic aquifer, which is not uncommon in the field (e.g. Jakobsen and Postma 1999; Kirk et al. 2004; Park et al. 2006). These reactions however, were likely temporary given that the

Fe⁺² plume propagated down-gradient and away from ongoing sulphate reduction.

The onset of methanogenesis is believed to have occurred sometime during the Transition Period since low to moderate CH₄ levels were first observed in each monitoring well on day 109 (not shown, but no CH₄ was detected in PGS during Stage 1, Figure 4.5, t = 67 days). From the Transition Period, CH₄ levels continued to steadily increase with distance down-gradient and with time (e.g. Figure 4.5, t = 187 to 300 days); with maximum CH₄ concentrations up to 943 μ M (e.g. MW3 at 130-cm depth) on day 300. These results demonstrate greater rates of CH₄ generation with time and up-gradient expansion of the methanogenic zone during Stage 2. They were also indirectly corroborated by measurements of decreasing bacterial cell abundances (based on phospholipid fatty acid (PLFA) analysis) on biofilm units hung in the HT and MWs over the same time period (Figure A4.2, reproduced from Clay 2014). Methanogens are archaeal organisms with different lipid membranes than measured with the PLFA analysis used. Therefore, the inverse trend in bacterial abundance compared to the CH₄ distributions is suggestive of a shift to an increasingly methanogenicdominated microbial community (Clay 2014).

Passive gas sampler analysis also revealed substantial H_2 levels in the monitoring wells during the experiment (Figure 4.5). H_2 commonly accumulates at trace amounts in biogeochemically-active groundwater as its redox state becomes progressively more reducing, with maximum concentrations (< 100 nM) persisting during methanogenesis (e.g. Lovley et al. 1994). However, H_2

concentrations measured during Stage 1 ranged from 3000 to 60,000 nM and thus, were near or above the reported inhibitory limit (8000 nM) for fermentation based on laboratory experiments (Wiedemeier et al. 1999). Elevated H₂ accumulation may reflect continued fermentation due to high input hydrocarbon loadings (mainly ethanol) following the complete utilization of the entire electron acceptor pool (i.e., NO₃⁻, Mn⁺⁴, Fe⁺³ and SO₄⁻²) in the absence of a microbial consortium capable of methanogenesis. In fact, H₂ concentrations were much lower in Stage 2, ranging from 0 to 24,000 nM, after methanogenesis was established. Spatially, H₂ levels typically decreased with distance down-gradient (e.g. Figure 4.5, *t* = 67 days), possibly due to reduced production by fermentative microbes (possibly due to inhibitory issues) or increased uptake by other microorganisms; potentially complicated by mass loss as a result of partitioning into a gas phase and/or solid phase sorption processes.

In summary, along the groundwater flow path, the redox state generally evolved from denitrification to methanogenic conditions as the more thermodynamically favoured electron acceptors were preferentially utilized for hydrocarbon degradation (Wiedemeier et al. 1999). In addition, redox zonation within the test lane correlated well to the spatial hydrocarbon losses, proceeding to progressively reducing conditions in smaller distances down-gradient (i.e., less time) where input hydrocarbon loadings were highest (e.g. shallower depths during Stage 1 compared to Stage 2, Figure 4.3A, t = 67 vs. 187 days), likely due to greater degradation. Thus, it is clear that variation in hydrocarbon inputs and

microbial controls on redox zonation led to a dynamic biogeochemical evolution within the synthetic aquifer.



Figure 4.5: Dissolved gas compositions (% by volume) from Stage 1 (t = 67 days) and Stage 2 (t = 187 and 300 days) in each monitoring well at two depths, 60 and 130 cm below the sand surface. The average dissolved gas composition of the source groundwater (*GW*) is included at top for reference. Note that the pie chart positioning is approximate relative to actual monitoring well (*MW*) locations.

4.3.2.3 Changes in Total Dissolved Gas Pressure (P_{TDG})

Of major interest to this study, was the generation of biogenically-derived dissolved gases, which can be cumulatively measured using a total dissolved gas pressure (P_{TDG}) sensor. The source water P_{TDG} remained fairly steady over the duration of the experiment (Figure 4.6), at values less than P_{atm} due to the utilization of O_2 by ammonium oxidation (refer to Section 4.3.1). Within the aquifer however, a large increase (~ 35 kPa) in P_{TDG} , at both depths, was first captured at MW1 (e.g. shaded section in Figure 4.6) soon after hydrocarbon injection commenced. It is possible that a portion of this initial rise was due to the introductory IW spike, originally in equilibrium with the atmosphere, though its effect was likely temporary (< 2 days) once it was flushed out by source water, and yet P_{TDG} within the aquifer remained elevated. Thus, these data reveal rapid and sustained production of dissolved gases, signifying the inception of biodegradation immediately following the initial hydrocarbon release. This is the first reported application of P_{TDG} sensors for continuous monitoring of the onset of microbial hydrocarbon degradation in contaminated groundwater.

These P_{TDG} changes were expected to reflect the production of the less soluble gases, such as N₂ and CH₄ (Table 4.1). In contrast, the generation of CO₂ and H₂S were anticipated to have negligible impacts on total dissolved gas pressure given their relatively high aqueous solubilities (Table 4.1) and/or their tendencies to undergo chemical speciation. For instance, the concurrent dissociation of produced CO₂ to ionic species can induce significant DIC increases (recall Sub-Section 4.3.2.1) but as a result, maintain low dissolved CO₂

levels. In fact, maximum contributions of CO₂ and H₂S production to P_{TDG} were estimated to be less than 2.0 kPa cumulatively at 25°C, based on the highest CO₂ levels measured in the *PGS* and the input SO₄⁻² concentrations. Furthermore, the absence of methanogenesis at early times (i.e., during Stage 1, Figure 4.5, *t* = 67 days) suggests that the initial increase in groundwater P_{TDG} was mainly due to substantial N₂ production via heterotrophic denitrification. Fermentation may have contributed to a small degree, with maximum H₂ levels measured at *MW1* (Figure 4.5, *t* = 67 days). Calculations indicate that the input NO₃⁻ concentrations were sufficient to cause this magnitude of increase in P_{TDG} , assuming complete conversion to N₂ gas with negligible nitrogen assimilation for microbial biomass (Equation 3, Table A4.1).

Following the initial P_{TDG} increase shown in Figure 4.6, subsequent P_{TDG} measurements (t > 60 days) closely mimicked the calculated bubbling pressure (P^*_G), approximated here as P_w (= $P_{atm} + \rho gh$; Equation 4); demonstrating minimal influence of capillary pressure in this system, consistent with a coarsegrained sand. In addition, fluctuations in groundwater P_{TDG} and P^*_G with changes in P_{atm} , can indicate equilibration with a gas phase in shallow, unconfined aquifers (Chapter 3; McLeod et al. 2015); and thus, suggests gas phase formation within the initially fully water-saturated zone. This pattern was observed from the outset for sensors in the zone with initial trapped gas (not shown). Therefore, beyond the initial increase, the P_{TDG} probes did not provide any additional insights into later-time patterns of biogenic gas production, including the potential for gas phase growth. Indeed, the presence of a gas phase can buffer out any changes in dissolved gas concentrations due to biogeochemical reactions and regulate groundwater P_{TDG} at the local trapped gas pressure (i.e., P_G which is approximately equal to P^*_G in this case, recall Equations 1 and 4 in Section 4.1.1). These results indicate a limitation to the use of P_{TDG} sensors for monitoring biodegradation in areas with trapped gas, for example, within the zone of the fluctuating groundwater table.



Figure 4.6: Early-time changes in total dissolved gas pressure (P_{TDG}) for the head tank (HT) (blue lines, 0 cm down-gradient) and monitoring well 1 (MW1) (red and orange lines, 115 cm down-gradient) at two depths: 60 cm (lighter shade) and 130 cm (darker shade). Also shown are the barometric pressure (light gray line, P_{atm}) and the calculated bubbling pressures (medium grey line = 60 cm depth, black line = 130 cm depth, P^*_G). Shaded section highlights breakthrough of microbial gas production associated with the initial release of hydrocarbon contamination, initiating the experiment. Note data gaps indicate periods of equipment maintenance.

4.3.3 Trapped Gas Behaviors and Related Processes

A residual gas phase was present in the tank prior to the start of the experiment (Figure 4.7A, t = -37 days) as a result of the previous study on trapped gas dissolution (Chapter 3: McLeod et al. 2015). A zone (or wedge) of near-zero gas contents (i.e., within measurement ability of TDR, approximately 0.5% of bulk volume) was formed adjacent to the HT, while within the persisting quasi-saturated zone, the initial gas contents steadily decreased with depth (from approximately 7.6 to 2.5% of the bulk volume). Following the onset of hydrocarbon biodegradation, measureable changes in gas contents were observed, as presented in Figure 4.7A for several key times during the experiment (a more continuous evolution of trapped gas observations at various times, corresponding to tank sampling events, are shown in Figure A4.3 in Appendix 2). Cumulative changes were highlighted by plotting the net difference in gas saturations (gas content / porosity) at a given time from the initial distribution measured prior to the hydrocarbon release (Figure 4.7B). Also considered were the monthly rates of change in trapped gas saturations, which reflect the change in saturation over a single pore volume of groundwater passed (Figure 4.7C or Figure 4.3H). Note it is quite possible that the distributions in gas contents (or gas saturations) were more variable in space (i.e., patchy), especially along the length of the tank, than portrayed in Figure 4.7 (or Figure A4.3) for which linear interpolation was applied between the limited data points.


Figure 4.7: Spatial patterns of trapped gas contents (A); the net difference in trapped gas saturations from initial distribution (B); and monthly rates of change in gas saturations (C) at key times during the experiment: prior to hydrocarbon contamination (t = -37 days), during Stage 1 (t= 67 days), Stage 2 (t = 187, 230 and 300 days) and following hydrocarbon contamination (t = 370 days). For a more complete experimental sequence refer to Figure A4.3 in Appendix 2. Interpolation between the TDR probes (diamond symbols) was performed using linear triangulation (exact interpolator) in Surfer Software (Golden

4.3.3.1 Progression of Gas Phase Changes

A rapid start to biogenic gas production, indicated by the increase in P_{TDG} at MW1 (Figure 4.6), led to subtle increases in gas contents within the first five days of the experiment (not shown). These increases were restricted to a few TDR probes located at shallow monitoring points (\leq 105 cm below the sand surface) immediately down-gradient of the HT (< 200 cm) and were abundantly clear within 2.6 pore volumes of groundwater passed (Figure 4.7A and B, t = 67days). It is likely that gas contents also increased in the un-instrumented area between the IWs and the first TDR array, which potentially contributed to the bioclogging issues (Section 4.3.1). Interestingly, gradual and sustained decreases in gas saturations were also observed at several TDR probes (\geq 205 cm down-gradient of HT) throughout Stage 1. Maximum declines, up to 6.6% less of pore volume (e.g. 45 cm depth, 205 cm down-gradient of HT in Figure 4.7B, t = 67 days), appeared to coincide with the transition area from low to high gas contents, that is, the boundary between the original dissolution wedge and persisting quasi-saturated zone. Thus, patterns of gas phase growth and trapped gas loss were both expressed during this period even in the presence of significant hydrocarbon degradation (refer to Sub-Section 4.3.2.1).

By Stage 2, the amounts of trapped gas were substantially greater (e.g. Figure 4.7A, $t \ge 187$ days) and growth appeared more widespread throughout the aquifer (Figure 4.7B), now also occurring at deeper depths and further down-gradient of the *IWs*. Gas saturations at this time were above their initial values over the majority of the tank, except at a few very shallow monitoring points

immediately down-gradient of the *IWs* (persisting blue zone in Figure 4.7B). Over time, gas contents at nearly all monitoring locations continued to increase, with larger changes occurring at the back of the tank. However, on average maximum trapped gas contents never exceeded 9.5% of bulk volume even during continued biogenic gas production. This may indicate that vertical gas phase mobilization (ebullition) was limiting continued gas phase expansion under conditions of sustained microbial gas generation (discussed further in Sub-Section 4.3.3.2). As a result, a zone of maximum gas contents (> 9.0% contour, Figure 4.7A, t = 229 - 300 days) developed approximately 320 cm down-gradient of *HT*, expanding from multiple locations.

On the last day hydrocarbons were added to the *IWs*, measured trapped gas saturations had increased by up to 10.8% of the pore volume compared to initial conditions (see Figure A4.3B, t = 328 days). These increases filled in the initially fully water-saturated zone created during the previous tank study (see Chapter 3; McLeod et al. 2015) and resulted in the development and considerable expansion of the maximum trapped gas zone, which covered approximately 25.5% of the monitoring area (i.e., the interpolated area defined by the *TDR* probes) by day 328. Overall, these results directly show for the first time significant *in situ* gas phase development, expansion and accumulation associated with hydrocarbon degradation (i.e., dissolved gas production) within natural porous media at near field-scale.

Beyond bulk changes, the monthly rates of change in gas saturations were highly dynamic and transient throughout the experiment (refer to Figure

4.3H or A4.3C for more continuous evolution of rates). Often there were periods when parts of the aquifer were experiencing large increases in gas saturations (> 2.0% of the pore volume per month) but were separated by areas of relatively stable or even slowly declining gas saturations (e.g. Figure 4.3H, t = 67 or 229 days). Likewise, sudden shifts from increasing to decreasing gas saturations, or vice versa, were observed for a given area over less than one pore volume of groundwater passed (e.g. compare 126 days vs. 147 days in Figure 4.3H). This illustrates substantial spatiotemporal variability, including unexpected and significant declines in gas saturations (i.e., trapped gas loss over a variety of time scales), in the multidimensional pattern of gas phase growth within the biodegradation zone. This suggests complex changes in the factors influencing trapped gas behaviors were occurring; these factors, both biogeochemical and physical processes, will be discussed in Section 4.3.4.

Finally, in the absence of hydrocarbons (t > 330 days) and significant biodegradation (i.e., dissolved gas production), the trapped gas then started to dissipate into the aqueous phase, captured as declining gas saturations (e.g. 105-cm probe, 320 cm from *HT* in Figure 4.8). This occurred at many locations in the tank, but was greatest along the bottom edge of the high gas content zone (i.e., high gas saturation boundary; Figure 4.7C, t = 370 days), where dissolution rates were highest. This pattern of dissolution deviates from the conceptual model developed for horizontal flow conditions during the previous tank study (see Chapter 3; McLeod et al. 2015). A possible explanation for this dissolution pattern will be provided in Sub-Section 4.3.3.3.

4.3.3.2 Evidence of Ebullition

Increasing gas contents at several of the TDR locations eventually leveled off (e.g. 15-cm to 75-cm probes in Figure 4.8) despite evidence of sustained hydrocarbon degradation and biogenic gas production (i.e., largely methane, Figure 4.5, $t \ge 187$ days). This upper limit to trapped gas accumulation suggests that vertical advection of the gas phase was occurring with continued dissolved gas production balanced by free-phase gas release away from these locations via ebullition. Ultimately, this led to the development of a maximum trapped gas zone (e.g. > 9.0% contour in Figure 4.7A, t = 229 - 300 days), where average gas contents never exceeded 9.5% of the bulk volume \pm 1.2% (or 27.0% of the pore volume). This maximum gas content level is consistent with reported critical gas saturations (S_{CG}), representing the storage threshold for the onset of gas phase advection (Du and Yortsos 1999), for coarse-grained materials (e.g. Amos and Mayer 2006b; Istok et al. 2007; Hegele and Mumford 2014). Homogeneous porous media are unable to retain greater gas volumes than the S_{CG} because the local capillary forces that trap the gas ganglia *in situ* are exceeded by buoyancy forces (Tsimpanogiannis and Yortsos 2004). It was anticipated that had the experiment been extended and biogenic gas production continued past 330 days, gas contents at all of the TDR locations, such as the 105-cm, 135-cm and 165-cm depths shown in Figure 4.8, would have eventually achieved the S_{CG} ; and resulted in the expansion of the maximum trapped gas zone throughout the test lane.



Figure 4.8: Characteristic temporal evolution of continuous trapped gas contents (% of bulk volume) at each monitoring depth: 15 cm (light blue), 45 cm (dark green), 75 cm (blue), 105 cm (green), 135 cm (navy blue) and 165 cm (light green), relative to both experimental Stages and the Transition Period (shaded gray section). The vertical dotted line designates when the hydrocarbon additions to the injection wells ended (t = 330 days). Gray tab indicates the average value for the critical gas saturation (S_{CG}) in M49 sand, representing the storage threshold for onset of gas phase mobilization. Note this data is from various transects (i.e., different distances down-gradient of the *HT*).

When the S_{CG} was achieved episodic oscillations in gas content above instrument variability ($\leq 0.5\%$ of the bulk volume) were commonly observed (e.g. 15-cm and 45-cm probes in Figure 4.8). These occurred on a time scale (several hours) that could not be explained by gas phase growth coupled with dissolution (the latter typically occurring over months to years, e.g. McLeod et al. 2015). On the other hand, the vertical advection of a gas phase (ebullition) can account for sudden and rapid trapped gas loss (e.g. Sihota et al. 2013). Thus, each oscillation, a rise and sharp decline, is characteristic of an individual ebullition event, that is, the slower expansion of the gas phase due to dissolved gas production, followed by rapid fragmentation and vertical mobilization of gas ganglia (or loss of gas) at a given location, as observed by numerous laboratory studies (e.g. Roosevelt and Corapcioglu 1998; Geistlinger et al. 2006; Roy and Smith 2007; Mumford et al. 2009a; 2009b). It should be noted that the ability of *TDR* to resolve or capture the pore-scale nature of ebullition was perhaps limited due to coarse log rates (every 2 - 6 h) and averaging along the full length of the probes (30 cm long), which may have experienced multiple points of gas release at varying times. These observations however, still support the assertion that ebullition was occurring in the synthetic aquifer and therefore, minimizing the extent of trapped gas accumulation during sustained biodegradation.

Whereas, gas contents generally did not exhibit oscillations indicative of ebullition prior to attaining the S_{CG} . However, some exceptions were observed. For example, the *TDR* probe at the 135-cm depth along the third *in situ* array (Figure 4.8) showed oscillations during the Transition Period (t = 93 - 164 days). In these cases, oscillations were attributed to localized pockets of maximum gas saturations situated along only a partial section of a *TDR* probe. As a result, the measured gas content, representing the average value along the full-length of the *TDR* probe, would be less than S_{CG} but could still reveal changes due to any ebullitive losses along partial lengths of the probe. These observations suggest gas phase growth (accumulation) and/or release variability within the homogeneous sand at a scale < 30 cm. This may be due to incomplete lateral mixing of the plumes, leading to variable biodegradation across the width of the

tank, or other variability in capillary pressure thresholds and/or microbial populations.

The advective losses during an ebullition event (i.e., amplitude of an oscillation) in the synthetic aguifer were consistently small, typically around 1.5% of the bulk volume. This is characteristic of uniform, coarse-grained sands with low capillary pressure thresholds (Mumford et al. 2009b), though this small difference may also reflect effects of gas cluster coalescence following gas ebullition from below (Geistlinger et al. 2006; Mumford et al. 2009a; 2009b). Ebullitive volumes are expected to be more variable and larger as pore-size distributions increase and grain sizes decrease since greater expansion is required for gas phase mobilization as P_c thresholds increase (e.g. finer, poorly sorted materials, Tsimpanogiannis and Yortsos 2004). In addition, at a given rate of gas production, the frequency or occurrence of mobilization will also be lower as P_c increases in comparison to the synthetic aquifer (Mumford et al. 2008). Thus, in real aquifers, ebullitive losses will likely be more dynamic and variable from place to place due to natural spatiotemporal differences in biogeochemical conditions (i.e., type and rate of gas production) and aquifer properties.

4.3.3.3 Changes in Hydraulic Conductivity and Groundwater Flow

Relative conductivity ($K_r = K_{qs}/K_s$) relates the quasi-saturated hydraulic conductivity (K_{qs} , Faybishenko 1995) for trapped gas to the saturated hydraulic conductivity (K_s). Gas phase measurements (daily median) derived from *TDR* were used to estimate the K_r at each monitoring location using K_r vs. gas

saturation (S_G) data from 1-D column tests with the BARCO M49 sand and relevant data from Marinas et al. (2013) (see Figure 2.1 and Chapter 2 for more details). The minimum K_r after 328 days of hydrocarbon contamination was calculated as 0.47 (Figure 4.9B), and was found within the zone of maximum trapped gas contents (Figure A4.3A, t = 328 days). Indeed, a value of approximately 0.5 was applicable to all locations that achieved maximum saturation (S_{CG}), which in some cases was maintained for more than 100 days (e.g. 15-cm and 45-cm probes, 320 cm down-gradient of HT in Figure 4.7A, t =229 days to the end of the experiment). These results demonstrate that the maximum change in hydraulic conductivity (K) due to biogenic gas generation in this homogeneous coarse-grained sand (i.e., from zero to a maximum gas content of 9.5%) was restricted to a factor of 2 due to the onset of gas mobilization at S_{CG} . Ebullition-minimized impacts on K have also been observed in the laboratory experiments of lstok et al. (2007) and Jeen et al. (2012).

The first (t = -37 days, A) and final (t = 328 days, B) K_r fields provided in Figure 4.9 also show that only slight differences in K_r developed at each location through time during the experiment. This is partly due to limited biogenic gas production in some areas of the tank which induced relatively minor increases in gas contents. In fact, some gas saturations measured remained well below S_{CG} throughout the experiment, such as the *TDR* probes located within the original fully-saturated zone (e.g. 165-cm probe in Figure 4.8). Greater gas phase changes up to S_{CG} may have occurred at these locations if hydrocarbon contamination and subsequent dissolved gas production had continued past 328 days. Alternatively, it is also partly the result of pre-existing trapped gas (i.e., up to 7.5% of bulk volume prior to expansion to S_{CG} , Figure 4.7A, t = -37 days) due to a water table fluctuation, which may be a common condition at contaminated field sites. Therefore, within the zone of the fluctuating water table, changes in *K* will likely be limited by both persisting quasi-saturation (initial trapped gas) and the maximum saturation threshold (S_{CG}) associated with ebullition.



Figure 4.9: Relative hydraulic conductivity ($K_r = K_{qs}/K_s$; dimensionless) fields within the test lane before hydrocarbon contamination (t = -37 days, A); and at the end of the biodegradation experiment (t = 328 days, B). Contouring interval is 0.05. The open diamond symbols mark the locations of the *TDR* probes. All data was interpolated using a linear triangulation grid method in Surfer Software (Golden Software).

Greater hydraulic conductivity changes with gas phase expansion are expected for finer materials because of higher S_{CG} resulting from the larger capillary forces associated with the smaller pores (Tsimpanogiannis and Yortsos 2004); and especially in the presence of real-world aquifer heterogeneity. Indeed, within heterogeneous porous media, horizontal lenses or layering can act as capillary barriers, hindering vertical gas phase advection during biogenic gas production. Over time, substantial gas volumes can accumulate into gas phase pools on the underside of the capillary barriers (e.g. Glass et al. 2000); creating significantly higher gas saturations than measured here. Furthermore, any compounding *K* effects potentially associated with biodegradation, such as microbial biomass build-up and/or mineral precipitation (e.g. Baveye et al. 1998), were not considered in this study and thus, reported changes in *K* may have been underestimated. Overall, biogenically-derived hydraulic conductivity reductions may be greater in natural groundwater systems.

Previous studies have shown that similar trapped gas-induced changes in *K* (e.g. same order of magnitude, Soares et al. 1991; Schroth et al. 2001; Zhang and Gillham 2005; Amos and Mayer 2006a) can still significantly alter groundwater flow patterns via reduced flow or flow-bypassing in and around areas with the lowest *K*. Evidence of flow field distortion within the synthetic aquifer included the pattern of trapped gas dissolution that developed after hydrocarbon injection ceased and dissolved gas production diminished. For horizontal flow conditions, it was expected that dissolution would occur where the inflowing, under-saturated groundwater (i.e., $HT P_{TDG} < P_{atm} < P_G$, refer to Figure 4.6) first contacts the gas phase, at the injection wells in this case. Resultant mass transfer from the trapped gas would then saturate the groundwater with dissolved gases (raises the groundwater P_{TDG} to P_G). This, according to Henry's

law, would inhibit the dissolution of down-gradient trapped gas, which would be at the same P_G (Klump et al. 2008; McLeod et al. 2015). Note, very slight dissolution may still occur down-gradient for mixed-gas systems and where kinetic mass transfer is important (e.g. Holocher et al. 2003; Balcke et al. 2007), though this is not likely to be of major significance here.

Alternatively, the passing groundwater may continue to dissolve a gas phase if P_G increases along the flow path. This can result from a downward, vertical component to the flow (Holocher et al. 2003; Klump et al. 2008), given that P_G increases at greater P_w . Therefore, the greater rates of dissolution within the middle of the tank rather than at the front end (e.g. Figure 4.7C, t = 370days), imply that downward refraction or deflection of the flow lines occurred at the low-K zone boundary (also referred to as high gas saturation boundary in Sub-Section 4.3.3.1), where the spatial changes in K were steepest (i.e., tight K_r contours in Figure 4.9B). It is hypothesized that some form of this distortion to the horizontal groundwater flow field was likely present throughout the experiment given the initial presence of trapped gas in the tank (lower K_r values at shallower depths down-gradient in Figure 4.9A), that is, the persisting guasi-saturated region (recall Figure 4.7A, t = -37 days, Section 4.2.1). However, flow line deflection may have been dynamic, shifting as this low-K zone expanded laterally and experienced increasing gas saturations (e.g. to S_{CG}) over time.

The diversion of groundwater flow around regions affected by trapped gas may further complicate the management of contaminated sites by prolonging the dissolution and subsequent release of NAPL contamination from source zones, impacting microbial biodegradation rates and source zone longevity (Schroth et al. 2001; Amos and Mayer 2006a); in addition to potentially diverting remediation fluids (e.g. oxidants and nutrients) and tracers away from target zones (Li and Schwartz 2000; Schroth et al. 2001) or groundwater flow around permeable reactive barriers (Fryar and Schwartz 1998; Kamolpornwijit et al. 2003), impairing remediation efforts. Furthermore, this process may promote gas phase persistence in the low-*K* zone once hydrocarbon degradation and biogenic gas production diminish (Holocher et al. 2003; McLeod et al. 2015). It is also possible that this process may impact patterns of trapped gas growth during biodegradation.

4.3.4 Factors Affecting Variability in Trapped Gas Changes

4.3.4.1 Changes in Source Zone Configuration

Some of the temporal variability in the spatial pattern of gas phase changes (Figure 4.3H), introduced in Section 4.3.3, was linked to differences in hydrocarbon mass input (as a result of *IW* bioclogging, Section 4.3.1), impacting the occurrence and overall extent of biodegradation (or dissolved gas production). In fact, increases in gas saturations seemed largely restricted to shallow areas during Stage 1 when the hydrocarbon input was mainly shallow (e.g. Figure 4.3A and H, t = 42 - 67 days). Meanwhile, several deeper areas experienced trapped gas increases at later times (Stage 2) once the hydrocarbon source was predominantly deep (Figure 4.3A and H, $t \ge 187$ days). Therefore, spatially- and temporally- variable source zones and resultant contaminant plume

configurations, which are not uncommon at contaminated sites (as briefly mentioned in Section 4.3.1), will inherently result in complex patterns of trapped gas changes during natural attenuation.

4.3.4.2 Nitrate Attenuation and the Potential for Denitrification

It appeared that denitrification was initiated very guickly following hydrocarbon introduction, as nitrate concentrations declined sharply just downgradient of the IWs (Figure 4.3C; note Stage 2 shallow trends are discussed in Sub-Section 4.3.4.4). This is consistent with reports of very minor acclimation periods associated with denitrifying bacteria, which appear to be ubiquitous in groundwater systems (refer to critical review by Rivett et al. 2008; and references therein). Indeed, near-complete utilization of the input NO_3^- pool occurred within the front section of the tank (Figure 4.3C; t = 42 - 89 days), where initial gas phase growth was largely confined (e.g. Figure 4.3H, t = 67 days). This suggests that the presence of nitrate, sustaining N_2 production via heterotrophic denitrification (coupled to hydrocarbon oxidation), and its absence downgradient, despite available hydrocarbon mass, was the main controlling factor of gas saturation increases during Stage 1. Although, it is possible fermentation also contributed to some degree, with maximum H_2 levels measured at MW1 (Figure 4.5, t = 67 days).

Based on these results, it was anticipated that this denitrification zone within the hydrocarbon plume would continue to be a major hotspot for gas phase expansion, especially following source water nutrient increases (i.e.,

greater input NO₃⁻ concentrations, Section 4.3.1). However, up-gradient increases in gas saturations during Stage 2 remained relatively subtle over time (e.g. typically < 1.0% increase per month, Figure 4.3H, t = 187 - 300 days). It is likely that other NO_3^{-} attenuation processes hindered gas production from the available nitrate. For example, immediately down-gradient of the IWs, at depth (i.e., \geq 75 cm below sand surface), sharp decreases in hydrocarbons, NO₃⁻ and NO_2^- (Figure 4.3A, C and D, t = 187 - 300 days) were still observed but were accompanied by concurrent increases in NH_4^+ (above to input concentrations, e.g. Figure 4.3E, t = 264 days). This indicates that ammonification, performed by fermentative bacteria, was also occurring (Equation 4, Table A4.1; also refer to Sub-Section 4.3.2.2). Consequently, denitrification likely only accounted for a proportion of the measured decrease in NO_3^- (and hydrocarbons) and thus, associated N₂ production occurred to a lesser extent. Therefore, measured gas saturations remained well below S_{CG} (e.g. 165-cm probe in Figure 4.8) with minor reductions in K (recall Sub-Section 4.3.3.3) due to limited biogenic gas production in this area of the tank throughout Stage 2. Although ammonification is not typically the dominant nitrate attenuation mechanism in natural groundwater systems (Rivett et al. 2008), it may be relevant at denatured ethanol spill sites where there is an abundance of highly labile organic substrates.

4.3.4.3 Development of Methanogenic Conditions

Following up-gradient nitrate attenuation, spatiotemporal changes in the gas phase were largely related to the initiation and distribution of

methanogenesis in the synthetic aquifer (Sub-Section 4.3.2.2). Unlike denitrification however, the onset of methanogenesis occurred after a 'lag phase', estimated here as approximately 90 days. Significant acclimation periods for methanogens are not uncommon in laboratory experiments and/or field studies. including petroleum- and ethanol- fuel impacted sites, but are highly variable and site-specific, ranging up to 5 years (e.g. Baedecker et al. 1993; Corseuil et al. 2011; Jerman et al. 2009; Nelson et al. 2010; Spalding et al. 2011). It may be that competition by more energetically-favoured reactions also played a role in this lag. For instance, observed CH_4 production appeared inversely related to iron (III) reduction, that is, as the iron mineral phase of the sand was depleted and dissolved Fe⁺² generation diminished (Figure 4.3F, $t \ge 187$ days), monitored CH₄ levels increased (Figure 4.5, $t \ge 187$ days) over time. This may suggest that iron (III) reduction out-competed methanogens for fermentation products (e.g. acetate and H₂) during Stage 1 (Figure 4.3F, t = 42 - 89 days). As a result of this lag, no significant increases in gas saturations occurred at down-gradient locations (generally > 155 cm from HT, Figure 4.3H, t = 42 - 89 days) in the absence of methanogenesis (Figure 4.5, t = 67 days) at early times since ongoing iron (III)- and sulphate- reduction (Figure 4.3F and G, t = 42 - 89 days) contributed negligibly to the groundwater P_{TDG} (recall Sub-Section 4.3.2.3).

Early in the Transition Period however, with the first detections of low to moderate CH_4 levels in each *MW* (day 109 not shown in Figure 4.5), sudden, rapid increases in trapped gas were observed throughout the tank (e.g. up to 4.0% increase per month, Figure 4.3H, t = 109 - 126 days). Furthermore, during

Stage 2, the most dramatic increases in trapped gas occurred predominantly at the back of the tank (\geq 320 cm down-gradient of *HT*, Figure 4.3H, $t \geq$ 187 days) around *MW3* where measured CH₄ levels were always greatest (Figure 4.5), consistent with higher rates of methanogenic activity (recall Sub-Section 4.3.2.2). Also of note, during this period of dominant methanogenesis, the greatest rates of increase in gas saturations tended to occur slightly down-gradient of the areas experiencing substantial hydrocarbon mass loss (compare Figure 4.3A to H, $t \geq$ 187 days). This suggests there was a lag between microbial degradation of the parent hydrocarbons and the complete transformation into the gaseous end products. This may reflect fermentation of the hydrocarbons in the plume, consuming ethanol and producing biodegradation intermediates (e.g. acetate and H₂), with some delay in space or time before the methanogens made use of these intermediates to produce CH₄, though this is not fully proven.

4.3.4.4 Alternative Gas-Producing Pathways

Interestingly, significant increases in trapped gas were not always linked to the biological oxidation of hydrocarbons. For instance, unexpected increases in gas saturations were measured shallowly (i.e., depths < 75 cm) and progressively down-gradient during Stage 2 (Figure 4.3H, $t \ge 187$ days) when the hydrocarbon source was predominantly deep (Figure 4.3A). Based on observed decreases in NO₃⁻ (and NO₂⁻ increases, Figure 4.3C and D) along the groundwater flow path coupled with SO₄⁻² increases above source water conditions (i.e., > 300 µM approximately, Figure 4.3G), it was hypothesized that

reduced sulphur species, such as H_2S and/or iron sulphide minerals, were used as alternative electron donors to reduce NO_3^- to N_2 gas in the absence of significant hydrocarbon contamination (Equations 2A and B, Table A4.1; also refer to critical reviews: Korom 1992; Rivett et al. 2008). The required sulphur species were likely created as a result of Stage 1 hydrocarbon degradation under iron (III)- and sulphate- reducing conditions (recall Sub-Section 4.3.2.2), with potential H_2S retained in the trapped gas phase and then slowly released back into the groundwater during Stage 2.

The resultant SO₄⁻² plume and associated trapped gas increases (Figure 4.3G and H, $t \ge 187$ days) were observed to slowly propagate down-gradient with time. Presumably, this was due to the ongoing depletion of the finite supply of reduced sulphur species and thus, the extent of autotrophic denitrification was likely declining over time. However, this process still represents a significant source of dissolved gas that was related to biodegradation but that could persist after hydrocarbon contamination has diminished. In addition, without it shallow increases in gas saturations may have been insignificant at the affected monitoring locations during Stage 2. This illustrates the complexity of gas phase growth associated with the variety of mechanisms available for biodegradation of hydrocarbons in a groundwater setting.

4.3.4.5 Vertical Deflections in Groundwater Flow

While increases in gas saturations within the biodegradation plume were anticipated, patterns of trapped gas loss were also observed over a variety of

time scales (i.e., a few days vs. several months; recall Sub-Section 4.3.3.1). For example, gradual declines in gas saturations (typically < 2.0% decrease per month), were observed down-gradient (> 70 cm down-gradient of HT in Figure 4.3H, t = 42 - 89 days) of the denitrification zone (Figure 4.3C) throughout Stage 1. This was attributed to trapped gas dissolution, though dissolved gas conditions were considered unfavourable (i.e., $P_{TDG} \ge P^*_G$ due to sustained denitrification based on Figure 4.6, Sub-Section 4.3.2.3) for horizontal flow conditions. However, just as was noted for the dissolution pattern observed after hydrocarbon injection was stopped (Sub-Section 4.3.3.3), the dissolution observed here was likely sustained via downward flow caused by flow line deflection along the zone of increasing trapped gas (i.e., shallower depths, downgradient in the original persisting guasi-saturation zone, also referred to as the low-K zone) (e.g. Figure 4.7B, t = 67 days). This illustrates how variation in the hydraulic conductivity (K) field associated with spatial variability in trapped gas contents within the synthetic aquifer, ultimately contributed to more variable patterns of trapped gas growth. Eventually, this dissolution ceased with the onset of methanogenesis during the Transition Period (e.g. Figure 4.3H, t = 109 days).

4.3.4.6 Ebullitive Impacts

Beyond changes in biogenic gas production, there is evidence that variation in the gas phase was also affected by trapped gas advection (ebullition) within the synthetic aquifer. Firstly, reduced rates of increase in gas saturations were observed over time (e.g. > 200 cm down-gradient of *HT*, Figure 4.3H, t =

187 - 300 days) even under conditions of continued biogenic gas production, where gas contents attained the maximum saturation threshold (S_{CG}) associated with ebullition (recall 15-cm, 45-cm and 75-cm depths in Figure 4.8), as discussed in Sub-Section 4.3.3.2. Thus, gas phase mobilization prevented further gas saturation increases and associated decreases in *K*, but only at times and locations where the S_{CG} was attained; and ultimately, contributed to temporal and spatial variability in trapped gas changes.

Secondly, it seems likely that rapid reductions in trapped gas contents observed in the tank during biodegradation were caused by ebullition rather than dissolution. An example of this was observed at 15-cm depth, 205 cm downgradient of HT during the Transition Period (e.g. Figure 4.3H, t = 109 to 147 days). At first, there were high rates of increase in shallow gas saturations (e.g. >3% per month, Figure 4.3H, t = 109 and 126 days) to S_{CG} ; which were then followed by sharp declines in gas saturations (e.g. > 3% per month, Figure 4.3H, t = 147 days) less than one pore volume of groundwater later. Such rates of decline were not observed during periods of known dissolution in the first tank experiment (Chapter 3); or in this experiment at early times (t = 10 - 92 days, Stage 1, Sub-Sections 4.3.3.1 and 4.3.4.5) and at the end in the absence of hydrocarbon contamination (t > 330 days, Sub-Sections 4.3.3.1 and 4.3.3.3). For comparison, the maximum rates of decrease in gas saturation per pore volume of groundwater passed at similar depths were 2.0% during dissolution versus 7.5% due to ebullition. This dramatic loss in trapped gas (~5.0% of the pore volume total) coincided with the shift in hydrocarbon input at the IWs from shallow to

deep (e.g. compare days 126 to 147 in Figure 4.3A). Therefore, it is hypothesized that gas phase advection continued at this location, despite a decline (or complete halt) in dissolved gas production due to much reduced hydrocarbon availability, resulting in a rapid net loss of trapped gas. This assessment could benefit from numerical modeling of the experiment, to better weigh the contributions of ebullitive losses and those of dissolution.

4.4 Summary and Conclusions

This pilot-scale tank experiment directly measured significant in situ trapped gas increases by up to 10.8% of the pore volume, at multiple locations over time due to microbial hydrocarbon (mainly ethanol) degradation under variable redox conditions, ranging from denitrification to methanogenesis. On average however, the maximum gas saturations never exceeded 27.0% of pore volume even during continued dissolved gas production. This was attributed to the vertical advection of the gas phase (ebullition) upon reaching a gas mobilization threshold, the critical gas saturation (S_{CG}). The data also revealed episodic oscillations in gas saturations around the S_{CG} , which are characteristic of individual ebullition events, that is, the repeated expansion, fragmentation and mobilization of the gas phase. Both observations support the assertion that trapped gas advection was occurring, balancing continued dissolved gas production with free-phase gas release away from affected locations and thus, maintaining S_{CG} over time. Prior research has shown that gas phase mobilization can expose formerly unaffected regions of the subsurface to contamination; and

pose significant explosion and asphyxiation risks due to gas accumulation in wells, soils and/or buildings. Although, the effect of ebullition on hydrocarbon vapour and biogenic gas transport within the synthetic aquifer and potentially to the atmosphere was not evaluated, new insights into the *in situ* nature of trapped gas accumulation and release in natural porous media at near-field scale were previously undocumented.

Based on laboratory column experiments, the maximum calculated change in hydraulic conductivity (K), associated with trapped gas growth in this homogeneous coarse-grained sand (i.e., from fully water-saturated conditions to S_{CG}), was restricted to a factor of 2. Gas phase mobilization maintained the S_{CG} during sustained biodegradation and thus, limited the overall decrease or impact on K. Although the trapped gas-induced reductions in K were not overly large, they still appeared to effectively alter the groundwater flow field. For example, the trapped gas dissolution pattern that developed after hydrocarbon injection (and dissolved gas production) ceased indicated that groundwater flow was deflected downward along the low-K zone boundary. Recall that flow by-passing around zones affected by trapped gas may impact remediation efforts at contaminated sites by extending NAPL source zone longevities and by diverting tracers, remediation fluids and groundwater flow from target zones including permeable reactive barriers.

Interestingly, while increases in gas saturations within the biodegradation plume were expected, significant declines in trapped gas were also observed. Thus, the overall, multidimensional pattern of gas phase growth exhibited

substantial spatiotemporal variability over the 330 days of hydrocarbon contamination. The main biogeochemical factors impacting trapped gas dynamics were changes in hydrocarbon plume input and microbial controls on redox zonation, determining the type gases produced during biodegradation and the resultant dissolved gas supersaturation, that is, the potential for trapped gas expansion. Gas phase advection (ebullition), in addition to the associated changes in hydraulic conductivity, impacting groundwater flow, also physically contributed to variable trapped gas growth patterns. Therefore, given the homogeneous nature of the synthetic aquifer and the degree of variability observed in the gas phase, trapped gas processes in contaminant plumes will likely be highly complex and dynamic in the natural groundwater systems, with important implications for site characterizations, management and remediation strategies.

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APPENDIX 2

Supporting Information for Chapter 4: A pilot-scale laboratory

investigation of gas phase dynamics within a groundwater

hydrocarbon plume

Table A4.1: Pertinent biological reactions from the nitrogen cycle with gaseous compounds identified in bold (Pauwels et al. 1998; Ryan et al. 2000; Rivett et al. 2008).

Reaction		Equation		
1	Nitrification	$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O$		
2A	Autotrophic Denitrification	$5H_2S + 8NO_3^- \longrightarrow 5SO_4^{-2} + 4N_2 + 2H^+ + 4H_2O_4^{-2}$		
2B	Autotrophic Denitrification	$5 \text{FeS}_2 + 14 \text{NO}_3^- + 4 \text{H}^+ \longrightarrow 10 \text{SO}_4^{-2} + 5 \text{Fe}^{+2} + 7 \text{N}_2 + 2 \text{H}_2 \text{O}$		
3	Heterotrophic Denitrification	$5CH_2O^a + 4NO_3^- + 4H^+ \longrightarrow 5CO_2 + 2N_2 + 7H_2O$		
4	Ammonification	$2CH_2O^a + NO_3^- + 2H^+ \longrightarrow 2CO_2 + NH_4^+ + H_2O$		

^a To simplify, CH₂O was used to represent organic matter; but other organic compounds, such as petroleum hydrocarbons, can also be oxidized.



Figure A4.1: Evolution of continuous bulk electrical conductivity measurements (mS/m) along the first *TDR* array (70 cm from the *HT*), at 15 cm (light gray, shallow), 75 cm (gray, middle) and 165 cm (black, deep) below the sand surface; following the initiation of three separate inorganic tracer test pulses, during the initial hydrocarbon release (t = 0 days, A); and when the lower (t = 75 days, B) or the upper (t = 348 days, C) portions of injection wells were affected by bioclogging during Stage 1 and 2, respectively. Note, this data was utilized for illustrative purposes only, comparative quantification and discussion of added tracer test complexities, such as density and/or tailing effects, were beyond the scope of this study.



Figure A4.2: Calculated bacterial cell abundances on collected biofilm units during Stage 2 based on phospholipid fatty acid (PLFA) analysis. Biofilm units consisted of porous telfon tubes (30 cm long × 3 cm in diameter) packed with sterilized glass wool. One unit was installed at the bottom of each monitoring well (*MW*) and the head tank (*HT*) for roughly 30 days before collection. Refer to Clay (2014) for full procedures regarding preparation, handling, storage and analytical analysis of the biofilm units; in addition to data interpretation and cell count calculations.





A) Trapped Gas Contents



B) Change in Gas Saturations from Initial



C) Monthly Rates of Change in Gas Saturations

-2 -1 0 1 2 3 4

% of Pore Volume per PV of Groundwater Passed

D) Relative Hydraulic Conductivity Values

0.50	0.60	0.70	0.80	0.90	1.00
				Dimensionless	

Figure A4.3: Spatiotemporal evolution of trapped gas contents (A); the net difference in gas saturations from initial distribution (B); the monthly rates of change in gas saturations (C); and finally the estimated relative conductivity values (K_r , D) throughout the test lane at key times during experimental duration (t = -37 to 370 days). Note that all dates provided correspond to a tank sampling event except for days 328 and 370; and that the Transition Period includes days 109 through to 164. Interpolation between the TDR probes (diamond symbols) was performed using linear triangulation in Surfer Software (Golden Software).

CHAPTER 5

Overall Conclusions and Recommendations
5.1 Concluding Summary

Natural and contaminated aguifers can have conditions of guasisaturation, leading to complex multiphase systems with variable gas-water interactions, biogeochemical conditions, hydraulic properties and transport processes. However, previous work detailing gas phase dynamics in groundwater systems have primarily been restricted to small-scale (< 1.0 m), laboratory experiments (e.g. Holocher et al. 2003; Amos and Mayer 2006; Istok et al. 2007; Klump et al. 2008) and/or peripheral field observations (e.g. Amos et al. 2005; Sihota et al. 2013). Therefore, this dissertation adopted a novel experimental approach using a highly instrumented, pilot-scale, laboratory tank to better examine the *in situ* nature of trapped gas dynamics over larger spatial and temporal scales. Gas saturations were directly measured with Time Domain Reflectometry (TDR) probes, which were coupled with dissolved gas and aqueous geochemical analyses. Note that the dissolved gas conditions were partly monitored using total dissolved gas pressure (P_{TDG}) sensors, an emerging tool for field-screening of trapped gas that has only been implemented at a few groundwater sites (e.g. Manning et al. 2003; McLeish et al. 2007; Roy and Ryan 2010). Thus, this dissertation has extended substantially beyond the previous body of laboratory work, providing maximum applicability to real-world conditions.

In total, two systematic experiments were conducted over 716 days, and the amount and quality of laboratory data collected is unprecedented at this larger scale. The key areas of investigation included i) trapped gas dissolution following a water table fluctuation (Chapter 3); and ii) gas phase dynamics, with

the potential for gas mobilization, in a groundwater hydrocarbon plume experiencing dissolved gas production via biodegradation (Chapter 4). Together, the outcomes of this innovative work emphasize the relevance of gas phase processes and their associated impacts in shallow groundwater systems.

5.2 Key Contributions

5.2.1 Advances in Trapped Gas Dissolution

During the first experiment, dissolution occurred as a wedge-shaped front propagating down-gradient in the tank over time, with enhanced dissolution at depth. In fact, front advancement at the deepest monitoring point was 4.1 - 5.7x faster than the measured propagation near the groundwater table. This dynamic, depth-dependent dissolution pattern was mainly attributed to increased dissolved gas solubility, as shown by the total dissolved gas pressure (P_{TDG}) measurements. However, an estimated 12% increase in guasi-saturated hydraulic conductivity (K_{as}) with depth, based on 1-D laboratory column results, also contributed to greater dissolution at depth. Both mechanisms were associated with gas phase compression, measured with TDR, at greater water pressures (i.e., greater depths below the water table). Comparisons of the measured to flux (q)-scaled (accounts for differences in K_{qs} with depth) dissolution front propagation velocities, confirmed that enhanced dissolved gas solubility at depth predominantly contributed to the two-dimensional pattern of trapped gas dissolution observed.

Overall, the dissolution front near the water table advanced 1.0 m downgradient in 344 days, suggesting that gas trapped shallowly will likely persist for significant periods of time, potentially on a timescale of years under horizontal flow conditions. The experimental results also indicated a more diffuse dissolution front compared to the sharp fronts reported in the literature from numerical models, indicating larger-scale mass transfer kinetics were involved even for this homogeneous coarse-grained sand tank. Finally, the utility of the P_{TDG} probes for detecting a gas phase and continuously monitoring its dissolution was also demonstrated. Given the ubiquitous occurrence of trapped gas in unconfined, shallow aquifers, simple on-site screening of P_{TDG} will be useful for a wide variety of groundwater applications, from recharge and paleoclimate studies to site characterizations and remediation techniques.

5.2.2 New Insights into Gas Phase Dynamics in Contaminant Plumes

In the second experiment, hydrocarbon (mainly ethanol) biodegradation occurred under variable redox conditions, ranging from denitrification to methanogenesis. Significant *in situ* increases in trapped gas, up to 11% more of the pore volume, were measured at multiple locations within the tank over 330 days. However, maximum trapped gas saturations never exceeded 27% of pore volume even during sustained biodegradation. This upper limit to trapped gas accumulation, representing a gas mobilization threshold (i.e., the critical gas saturation, S_{CG}), indicates that vertical advection of the gas phase (ebullition) was occurring; balancing continued dissolved gas production with free-phase gas

release away from affected locations. Consequently, the maximum reduction in K_{qs} associated with gas phase growth, based on laboratory column measurements of the gas saturation – K_{qs} relationship, was restricted to a factor of two. Although the trapped gas-induced changes in K_{qs} were not overly large, they still appeared to effectively alter the groundwater flow field, causing deviations from horizontal flow conditions.

Interestingly, while increases in gas saturations were expected within the biodegradation plume, significant declines in trapped gas were also observed. In fact, the overall multidimensional pattern of gas phase growth exhibited substantial spatiotemporal variability suggesting complex changes in the factors influencing trapped gas dynamics; these included changes in hydrocarbon plume inputs and microbial controls on redox zonation, in addition to ebullition and the changes to the groundwater field flow. Given the homogeneous nature of the synthetic aquifer and the degree of variability observed in the gas phase, trapped gas processes in contaminant plumes will likely be highly complex and dynamic in the natural groundwater systems. Furthermore, significant trapped gas accumulation and release have important implications for the fate and transport of groundwater contaminants and thus, further complicate site characterizations, management and/or remediation strategies.

5.3 Recommendations for Future Research

Direct measurement of the gas phase, in addition to the near field-scale and multidimensional nature of the research conducted for this dissertation

improved the current fundamental understanding of trapped gas dynamics in shallow groundwater systems, and their implications for groundwater flow, the fate and transport of volatile contaminants and dissolved gases. However, future pilot-scale tank experiments should expand upon the behaviours of the gas phase within degrading hydrocarbon plumes, such as the mechanisms of autogenic gas formation (exsolution), the influence of groundwater pressure patterns (i.e., depth-dependent effects) on subsequent gas phase expansion and movement, and better coupling of *in situ* vertical gas fluxes (or ebullitive losses) with surficial mass flux measurements during biogenic gas production. Furthermore, broader scale, overarching avenues of future laboratory research on the topic of trapped gas processes should include:

- 1) Conducting experiments in finer-grained porous media. Greater trapped gas saturations following water table fluctuations could result in longer trapped gas persistence and more spatially- variable dissolution patterns due to larger differences in the K_{qs} at depth than observed in this dissertation. In addition, the higher S_{CG} associated with finer media could produce a more extensive network of disconnected gas pathways, thus allowing more rapid transport of volatile compounds and biogenic gases towards the vadose zone during microbial hydrocarbon degradation.
- 2) Investigating more heterogeneous systems. Layered beds and lenses could cause major preferential dissolution channeling or fingering along coarser zones, creating highly complex and variable

trapped gas dissolution patterns beyond depth-dependent effects on mass transfer and changes in K_{qs} due to compression of the gas phase at higher water pressures, as seen in this dissertation. Also, in the presence biogenic gas production, trapped gas will likely accumulate as gas phase pools on the underside of horizontal layers or capillary barriers, creating significantly higher gas saturations than measured here and larger, more localized and sporadic gas mobilization events.

3) Further testing of the P_{TDG} probes. Areas of interest could include i) monitoring different biodegradation (natural attenuation) processes and associated dissolved gas consumption and/or production in contaminant plumes but in the absence of a trapped gas phase; ii) monitoring gas phase processes in different materials where the influence of greater capillary pressures could be resolved; and finally, iii) optimizing probe application to reduce probe noise during continuous monitoring.

In conclusion, laboratory experiments facilitate the collection of well-resolved spatiotemporal data and provide more simplified environments to investigate fundamental processes and to elucidate their controls and/or impacts. This research can then be applied to numerical modeling efforts and/or field studies in order to better understand real-world conditions or phenomena, such as trapped gas dynamics in natural and contaminated groundwater.

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