MOBILIZATION OF ENTRAPPED GAS IN CONTAMINATED GROUNDWATER

MOBILIZATION OF ENTRAPPED GASES IN QUASI-SATURATED GROUNDWATER SYSTEMS CONTAMINATED WITH BIOFUEL ADDITIVES

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Lay Abstract

The use of biofuel additives in gasoline and diesel fuels has become an attractive alternative to fully petroleum-based fuels to reduce the release of vehicular greenhouse gases to the atmosphere. As fuel spills and storage tank leaks continue to be a primary source of groundwater contamination, the appearance of biofuel additives in contaminated systems will appear below the subsurface as they continue to be administered to modern gasoline and diesel fuels. This work investigated the consequences of biofuel contamination of groundwater systems containing gas trapped within pore spaces through the use of laboratory experiments and numerical modelling. Contamination of these systems with different biofuel additives displayed a similar response, in which gas had mobilized from within pore spaces and released to the atmosphere. Mobilization of trapped gas in groundwater can alter the primary hydraulic properties that characterize a particular hydrogeologic system.

Abstract

Biofuel additives have been designed to reduce vehicular emissions to the atmosphere to limit the effects of greenhouse gases on global climate change. The chemical properties of common biofuel additives exhibit ideal characteristics for use in gasoline and diesel, while limiting emissions from exhaust. As biofuel additives begin to be administered regularly to gasoline and fuel sources, the compounds will appear in spill sites, posing a risk to groundwater sources. The interactions that occur between common biofuel additives and trapped gases below the water table were analyzed in this work to further understand the potential consequences on quasi-saturated groundwater zones. The behaviour of trapped gases contaminated with different biofuel additives were analyzed in laboratory experiments conducted in a two-dimensional flow cell to demonstrate the mechanisms of gas flow through a capillary barrier resulting from modified interfacial properties in the presence of a chemical surfactant. Contamination of gas-fluid interfaces by applied biofuel additives at the pore scale resulted in the breakthrough of gas through the capillary barrier. Gas migration terminated at a critical pool height proportional to the reduction in interfacial tension induced by the administered biofuel additives. To further demonstrate the relationship between interfacial tension and critical gas pool height, an interfacial tension-macroscopic invasion percolation model was developed to simulate the transport mechanisms and behaviours of gas flow when an immobile pool is contaminated with 1-Butanol. The findings in this study provide a fundamental understanding of the mechanisms and behaviours of gas mobilization in the presence of common biofuel additives.

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List of abbreviations

1-BuOH	1-Butanol
BTEX	Benzene toluene ethylbenzene xylene
CO	Carbon monoxide
EtOH	Ethanol
GHG	Greenhouse gases
IP	Invasion percolation
Iso-BuOH	Iso-Butanol
LNAPL	Light non-aqueous phase liquid
MTBE	Methyl tert-butyl ether
MIP	Macroscopic invasion percolation
MIP-IFT	Macroscopic invasion percolation-interfacial tension
NAPL	Non-aqueous phase liquid
PAH	Polycyclic aromatic hydrocarbon
P _C -S	Capillary pressure-saturation
PM	Particulate matter
t-BuOH	Tertiary Butanol
TEL	Tetraethyl lead

List of Symbols

P_c	capillary pressure (L)
σ	interfacial tension (MT ⁻²)
r	pore radius (L)
θ	contact angle
h _{gas}	height of gas pool (L)
P_c^{top}, P_c^{bottom}	capillary pressure at boundaries of gas pool (L)
g	acceleration due to gravity (LT ⁻²)
Δho	density difference of immiscible fluids (ML ⁻³)
N_{Bo}	bond number (-)
k	permeability (-)
N_{Ca}	capillary number (-)
q	darcy velocity (LT ⁻¹)
μ	viscosity (ML ⁻¹ T ⁻¹)
\bar{v}	average linear pore water velocity (LT ⁻¹)
Κ	hydraulic conductivity (LT ⁻¹)
η_e	effective porosity (-)
dh	hydraulic gradient (-)
dl	
D	hydrodynamic dispersion (L^2T^{-1})
α	dispersivity (-)
D^*	effective dispersion coefficient (L ² T ⁻¹)

С	concentration of aqueous solute (ML ⁻³)
x	depth of contaminant transport (L)
t	time (T)
$ ho_w$	density of water (ML ⁻³)
σ_{su}, σ_{w}	interfacial tension of the surfactant, interfacial tension of water
	$(ML^{-2}T^{-2})$
$ ho_b$	bulk density of soil sample (ML ⁻³)
$ ho_s$	density of soil solid (ML ⁻³)
η	porosity (-)
m_T	total mass of the sample (M)
V_T	total volume of the sample (L^3)
γ	weight of water (ML ⁻³)
H_s	height of the sand pack (L)
V_{add}	volume of surfactant added to the flow-cell (L^3)
V_{pool}	volume of the pool above the sand pack (L^3)
A	cross-sectional area of the flow-cell column (L^2)
L	distance of transport for the average particle (L)
a, b	parametric constants specific to 1-BuOH (-)
$\theta_w, \theta_{rw}, \theta_{sw}$	volumetric water content of water, residual water, saturated (-)
V_{sw}	volume of water in the sample when fully saturated (L^3)
ΔV_w	change in the water volume in the burette (L^3)
S_{w}, S_{wr}	water saturation, residual water saturation (-)
<i>n, m</i>	fitting parameters in the Brooks-Corey model (-)
α_i	inverse of the entry pressure in Brooks-Corey model (L ⁻¹)
P_d , P_e , P_t	displacement, entry, terminal pressure of the material (L)
λ	parameter representing the pore-size distribution of the media (-)
α	parametric constant ratio of terminal to entry pressure (-)
P_w	hydrostatic pressure (L)
T_t , T_e	terminal threshold, entry threshold (L)
h	height of water (L)
P_0	pressure at the top of the flow-cell domain (L)
H_{Co}, H_{θ}	height of the gas pool at different stages of contamination with
	surfactant, initial height of the gas pool (L)
$H_{F:I}$	contaminated pool height ratio

Declaration of Academic Achievement

I am the sole author of this thesis. I conducted all the laboratory experiments. I performed all the analyses of the laboratory experiments and wrote all of the thesis content about the laboratory experiments under the supervision of Dr. James E. Smith. I wrote the computer code used to perform the modelling work, conducted all of the numerical modelling simulations, analyzed the outcome of this work and contrasted the results of the modelling work with laboratory experiments under the research supervision of Dr. Kevin Mumford at Queen's University.

Chapter 1: Introduction and Research objectives

1.1. Background

A complete understanding of the hydrogeologic processes and interactions characterizing contaminated groundwater systems has become a critical subject in scientific literature due to the economic and social importance of potable aquifer systems and their limited availability as a natural resource. The looming risk of a global water crisis continues to threaten communities around the world as the demand for freshwater resources increases to sustain a growing human population (Hinrichsen & Tacio., 2002; Wada et al., 2010). Over 75% of the world's population relies on potable aquifer sources as a primary water resource, as surface water body availability decreases with overexploitation and contamination (Vrba & Van der Gun., 2004). In Canada alone, almost ten million people rely on groundwater as their primary water source for consumption and use in irrigation, farming, and mining (Rutherford., 2004). Although Canada has the one of the world's largest freshwater reserves, the risk of resource depletion continues to increase as consumption exceeds its replenishment (Hinrichsen & Tacio., 2002; Llamas & Custodio., 2002). Monitoring potable groundwater systems for various contaminant levels has become mandatory prior to use as a natural resource due to the common threat of contamination (Mackay & Cherry., 1989). Since leakage of petroleum products is one of the most common contaminant sources, there is a particular focus on the monitoring of groundwater constituents derived from gasoline and diesel fuels in contaminated systems (Mackay & Cherry., 1989; Corapcioglu & Baehr., 1987).

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Contamination below the subsurface during refining, distribution and storage of petroleum fuels and gasoline poses a severe risk to potable groundwater resources (Shih et al., 2004). In order to adapt to a changing climate, the compounds that comprise gasoline and diesel fuels have been modified to limit environmental impacts. It is expected that chemical constituents of modern gasolines will appear below the subsurface in contaminated spill sites. In 1990, the Federal Clean Air Act deemed the addition of fuel oxygenates in gasoline and diesel fuels mandatory in order to reduce exhaust and vehicular emissions to the atmosphere (Deeb et al., 2003; Schmidt., 2003; Shih et al., 2004). Methyl tert-butyl ether (MTBE) has been used as a preferable fuel oxygenate due to its low cost, high octane number, and optimized blending with gasolines (Deeb et al., 2003; Rakopoulos et al., 2010; Shih et al., 2004; Westphal et al., 2010). The use of MTBE in gasoline and fuels has been observed to successfully reduce atmospheric greenhouse gases (GHGs) emitted from vehicles. However, increased use of MTBE in gasolines and fuels, along with its high solubility in water and resistance to degradation, has made it one of the most frequently detected volatile organic compounds in petroleum contaminated groundwater sites (Schmidt., 2003). Human exposure to MTBE in drinking water has been linked to cancers, tumour development and reproductive toxicity, leading researchers to develop alternative oxygenate fuel additives (Hartley et al., 1999). Biofuel additives produced from natural sources and organic matter, including; ethanol, 1butanol, tertiary-butanol, and iso-butanol, are beginning to be implemented as an alternative oxygenate additive to MTBE (Christensen et al., 2011). These compounds function to reduce exhaust and vehicular emissions by enhancing fuel combustion

efficiency in engines, while limiting environmental repercussions with a high degradability in natural systems.

Understanding the hydrogeologic interactions of biofuel additives in groundwater systems becomes increasingly important as their use and application in gasoline and fuels continues. The chemical properties of biofuel additives render them excellent oxygenate additives (Liu et al., 2016). Their high oxygen content provides optimized combustion efficiency in vehicles, with an enhanced solubility in gasoline and fuels due to the presence of a hydrophobic hydrocarbon chain (Liu et al., 2016). These same chemical properties cause the compounds to exhibit behaviours similar to that of a chemical surfactant, in which upon encountering an interface between two immiscible fluids, the molecules will preferentially sorb and orient themselves along the interface (Ronen et al., 1989). These phenomena can have influences on the behaviour of immobile non-wetting fluids trapped below the subsurface, including NAPL residuals or trapped gases, by altering interfacial properties along the interface of immiscible fluids.

Trapped gases generated within the saturated zone can occupy up to 20% of pore spaces, acting as barriers to the flow of water in groundwater systems (Fry et al., 1997). Stabilized by retaining capillary forces, the presence of trapped gas bubbles and pools below the water table exhibit unique hydraulic properties different from that of a completely saturated system due to the added resistance to flow. As hydrogeologic parameters in field settings are often measured over a large aquifer volume, they represent an average of the system properties over the sample size during the time of measurement (Freeze & Cherry., 1979). Introduction of gases in a previously saturated groundwater system can result in; reductions in hydraulic conductivity (Faybishenko., 1995; Marinas et al., 2013), reductions in permeability (Orlob et al., 1958), increased dispersivity of solutes (Klenk et al., 2002), and over-estimation of specific yield and recharge (Gonçalves et al., 2020). Modification of groundwater properties due to the presence of chemical surfactants can lead to considerable changes in measured hydraulic parameters leading to possible misinterpretation and misrepresentation in field studies.

Studies have observed the effects of mobilization of trapped gases below the subsurface due to gas expansion in the presence of volatile compounds (Mumford et al., 2009; Roy & Smith., 2007), however, there are no studies in the literatures analyzing the impacts of surfactant contamination on the migration of trapped gases in a quasi-saturated porous medium.

1.2. Hypothesis and Research Objectives

Based on the dependence of trapped gas stability on capillary pressure of a confining medium, it was hypothesized that contamination of gas-fluid interfaces with biofuel additives will result in the mobilization of entrapped gases due to reduced capillary forces. It is was further hypothesized, that the migration of gas would terminate at a critical gas pool height, that would be proportional to the reduction in interfacial tension established at an interface, characteristic of the surfactant properties of the biofuel additives that contaminated the system. It was further expected that transport and migration of gas through a porous medium would be influenced by heterogeneity and variability in the pore size and saturation distribution of the capillary barrier, or confining region.

The objectives of this research were to 1. conduct a series flow-cell laboratory experiments to demonstrate the effects of contamination by different biofuel additives on the mobilization and migration of trapped gases in quasi-saturated groundwater systems; 2. demonstrate the key mechanisms driving gas flow through an initially saturated porous medium; and 3. understand the effects of subsurface variabilities on the flow of gas through porous medium. In experiments, unique hydraulic and physical properties were established to further understand the migration and transport of gas through a confining capillary barrier. Finally, this work focused on 4. the development and modification of an existing MIP model developed by Mumford et al. (2010) to incorporate concentration dependent interfacial tension changes on the mobilization of entrapped gas. Using the developed numerical model, 5. simulate the effects of interfacial tension reduction on the behaviours of entrapped gas in response to contamination of 1-butanol from flow-cell experiments and 6. conduct a sensitivity analysis to further understand the primary parameters effecting fluid transport in the contaminated system.

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Chapter 2: Literature Review

2.1. Entrapped gas in groundwater systems

2.1.1. Hydraulic properties of quasi-saturated groundwater systems

The multiphase flow phenomena and migration of gases through porous media has been studied extensively in both laboratory and field-based groundwater analyses due to the importance in characterization and investigation of potable aquifer systems (Dunn & Silliman., 2003; Faybishenko., 1995; Fayer and Hillel., 1986a.; Klump et al., 2007; Marinas et al., 2013; McLeod et al., 2015). Trapped gases have been observed to occupy up to 20% of the pore spaces in a porous medium, having an influence on the hydraulic flow and transport of solutes through groundwater systems (Fry et al., 1997). Entrapped gas below the subsurface has been defined as disconnected air that is immobile and discontinuous (Faybishenko., 1995). When gas displaces water in a saturated system, the saturation capacity of a porous medium is reduced to a residual value dependent on the volume of pores that are occupied by gas (Gerhard & Kueper., 2003). A porous medium comprised of air occupied pore spaces in the saturated zone can no longer be classified as "saturated", nor, as the unsaturated zone. These systems are defined as quasi-saturated due to the unique characteristics of the multiphase system, exhibiting positive gas pressures below the water table (Faybishenko., 1995; Klump et al., 2007; Marinas et al., 2013). This shallow region is often characterized as the quasi-saturated groundwater zone, in which entrapped gases can be sustained due to reduced hydrostatic pressures at lower depths (Holocher et al., 2003).

The hydraulic properties governing quasi-saturated systems differ considerably from saturated systems. The introduction of entrapped gases in a previously saturated system has the capacity to cause significant changes in hydraulic properties such as; permeability, hydraulic conductivity, recharge rates, and dispersivity (Faybishenko., 1995; Gonçalves et al., 2020; Klenk et al., 2002; Marinas et al., 2013; Orlob et al., 1958). Laboratory studies analyzing the change in hydraulic characteristics in the presence of entrapped gases have displayed a linear decrease in permeability with increased entrapped air content (Orlob et al., 1958). Pores occupied by gases are no longer conducive to the transport of fluids, acting as a barrier to flow of water and pore connectivity. As a result, fluids are limited in their ability to permeate through the pore space. The magnitude in which permeability decreases in the presence of entrapped gas is not only dependent on the size and volume of gas, but also the types of pores occupied by gas. Orlob et al. (1958) observed a greater sensitivity to grain size distribution, in which well graded media were more sensitive to the presence of trapped gas, resulting in larger decreases in permeability with increased gas saturation. As gas bubbles preferentially displace water out of larger pores, the reduction in permeability becomes significant, exhibiting a disproportional change in well graded media. These same effects has been demonstrated to result in a decrease in hydraulic conductivity of a quasi-saturated porous medium (Faybishenko., 1995; Marinas et al., 2013). The presence of trapped gases in an initially saturated porous media displayed decreases in hydraulic conductivity by a minimum of two-orders of magnitude (Figure 2.1, Faybishenko., 1995; Marinas et al., 2013).

The presence of gas-occupied pores in quasi-saturated systems has been demonstrated to modify the migration and transport mechanisms of solutes through a porous medium. Dispersivity of solutes through a system is increased in the presence of gases (Klenk et al., 2002). The presence of air immobilized in pore spaces causes an increase in tortuosity for advective fluids through pores that extends solute transport further in a medium. Furthermore, modifications to the amount of gas occupying pore space can lead to changes in the rate of solute and contaminant transport in groundwater systems.

The presence of gas in quasi-saturated systems has been demonstrated to significantly alter hydraulic properties. Omitting the effects and identification of trapped gases in groundwater characterization can lead to misinterpretation of multiphase flow processes in a quasi-saturated system. More recent analyses have suggested overestimation of specific yields and recharge rates in shallow unconfined aquifers as a result of dismissing effects of entrapped air on reduction of permeability and other aquifer properties (Gonçalves et al., 2020). Changes in entrapped gas content in quasi-saturated systems resulting from mobilization or dissolution could result in considerable alterations to groundwater properties and hydraulic characteristics, including permeability, hydraulic conductivity, and dispersivity quantification.

2.1.2. Generation of trapped gas below the subsurface

Atmospheric and chemically generated gases can become trapped within the saturated zone through several different processes. Natural mechanisms leading to the synthesis of gas in the quasi-saturated zone include soil swelling (Faybishenko., 1995), water table

fluctuations (Dunn & Silliman., 2003), and by-products of biological decomposition of organics (Orlob et al., 1958). Anthropogenically induced gas entrapment in the saturated zone has also been observed to result as a consequence of remediation technologies. Roosevelt & Corapcioglu (1998) observed the generation of trapped gas bubbles following air sparging in a glass-bead laboratory study, in which bubbles of a critical size were immobilized upon synthesis. Other studies have observed gas entrapment as a result of artificial recharge technology due to large fluctuations in hydraulic head on an annual basis (Cey et al., 2008). For gas to become trapped and remain immobile beneath the subsurface, transport through the porous media must be constrained.

Both transport and immobilization of immiscible fluids through saturated porous media depends on the capillary pressure established at an interface between twoimmiscible fluids (Berg., 1975; Fetter et al., 2017). Contact of two immiscible fluids at an interface results in the generation of a curved interface. The radius of curvature of the interface results from the difference in the strength of molecular attraction between like-molecules and unlike-molecules, generating a pressure difference across the boundary, recognized as capillary pressure (Fetter et al., 2017):

$$P_c = \frac{2\sigma \cos\theta}{R} \tag{2.01a}$$

$$P_c = \frac{2\sigma}{r} \tag{2.01b}$$

Where P_c (ML⁻¹T⁻²) is the capillary pressure, σ (MT⁻²) is interfacial tension at the gaswater interface, θ is the contact angle and R (L) is the pore radius. Assuming θ is constant in time, $\frac{\cos\theta}{R}$ can be expressed as r (L), which is the effective pore radius, which is treated here as the critical pore radius. The curvature of the interface generates a pressure difference between the two-fluids comprising the boundary:

$$P_c = P_{NW} - P_W \tag{2.02}$$

where P_{NW} (L) is the pressure of the non-wetting fluid, and P_W (L) is the pressure of the wetting fluid. The capillary pressure is also influenced by the wettability and surficial properties of the solids in which both fluids are in contact with, often quantified by the representative contact angle. The contact angle at a phase boundary is not static in mobile multiphase flow systems. The contact angle is dependent on the viscosity of the fluids, the velocity of the fluid flow, molecular behaviours at the fluid interface, surface roughness of the solid and the hysteresis of the system (Johnson et al., 1977). The contact angle of a migrating interface is variable depending on if it is advancing or receding, and thus is described as dynamic in flowing groundwater systems. Although recognized as a dynamic component in multiphase flow, throughout this study, contact angle was assumed to be a secondary effect impacting transport, in which interfacial tension was the primary parameter driving multiphase flow behaviours. Dynamic contact angle was embedded in capillary pressure measurements, and thus did not go unaccounted for.

In a multiphase system, transport of non-wetting fluid through saturated porous media is only possible when the capillary pressure exceeds the characteristic entry pressure, or resistance, of a proceeding pore (Gerhard & Kueper., 2003; Mumford et al., 2009). If the local pressures are unable to overcome resistance induced by capillary forces, transport of the non-wetting fluid will not occur. In an air-water system, buoyant forces, viscous forces and capillary forces are the primary force balance components

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dictating fluid transport (Figure 2.2; Berg., 1975; Mumford et al., 2009; Pennel et al., 1996; Roy & Smith., 2007). When buoyant and viscous forces are exceeded by capillary forces of proceeding pores, fluid transport is inhibited, and air will remain trapped. Gases will trap to a critical pool size characteristic of the porous media properties and hydrogeologic properties of the groundwater system (Mumford et al., 2009; Roy & Smith 2007):

$$h_{crit} = \frac{P_c^{top} - P_c^{bottom}}{\Delta \rho g}$$
(2.03)

where h_{gas} (L) is the height of the gas pool, P_c^{top} (ML⁻¹T⁻²) is the capillary pressure at the top of the gas pool, P_c^{bottom} (ML⁻¹T⁻²) is the capillary pressure at the bottom of the gas pool, g (LT⁻²) is the acceleration due to gravity, and $\Delta\rho$ (ML⁻³) is the density difference of air and water, synthesized based on force balance. The capillary forces that enable entrapment are directly dependent on the interfacial tension at the gas-water interface (Fry et al., 1997).

Gas can become entrapped in pore spaces by immiscible displacement or exsolution of gas from chemical reactions (Fry et al., 1997; Ronen et al., 1989). Gas bubbles can nucleate from exsolution out of water if the water is supersaturated with gases, in which a reduction in pressure or increase in temperature will establish a supersaturated system. To remain stabilized, forces acting to retain the gas must not be exceeded by countering forces. As a result, air bubbles and trapped gases are typically found in shallower depths of groundwater due to the reduced hydrostatic pressure acting on the gas volumes (Holocher et al., 2003). As hydrostatic pressures are increased with depth, increased pressures acting on the air will enhance gas transfer and provoke dissolution.

2.1.3. Geologic structures and stratigraphic features that facilitate gas entrapment

Mechanisms of non-wetting fluid entrapment may occur at both the pore scale and macroscopic scale, in which fluids become immobilized due to the resistance imposed by proceeding pores (Szymkiewicz et al., 2011). At the pore scale, small ganglion or residuals may become trapped as gases migrate towards smaller sediment grain sizes (Berg., 1975). Upon encountering smaller pores, transport through saturated media is inhibited due to the resistance caused by higher entry pressures required for the displacement of water by gas. Despite the importance of pore-scale trapping in porous media, this study focuses on the larger scale, macroscopic gas trapping generated from a stratigraphic capillary barrier.

Considerable volumes of trapped non-wetting fluids are commonly observed below heterogeneities and lenses characterized by contrasting hydraulic properties from the rest of the porous medium. Natural coarse sediment deposits surrounded by a finer sediment deposit act as blockades to non-wetting fluid transport (Dunn & Silliman., 2003; Rittenhouse., 1972; Szymkiewicz et al., 2011). This unique geology is often characterized as capillary barriers, air entry barriers, or permeability barriers. These stratigraphic traps limit vertical connectivity of available pore pathways to transport nonwetting fluids through a porous media by introducing a region of high resistance and high entry pressures characteristic of reduced pore size and contrasting geometry of pores and throats (Rittenhouse., 1972). For gases and non-aqueous phase liquids (NAPLs) to migrate through capillary barriers, opposing forces must overcome the higher resistant forces retaining the gas from mobilization.

Capillary barriers can be observed naturally in different geologic settings with unique depositional environments (Dunn & Silliman., 2003; Rittenhouse., 1972; Szymkiewicz et al., 2011). Rittenhouse (1972) classified and characterized several types of stratigraphic traps based on the sediment and geologic properties that inhibit migration of non-wetting fluids through a saturated media. This classification method allows more specific identification of common stratigraphic settings favourable for fluid entrapment defined by; facies-change traps, diagenetic traps, and traps adjacent to unconformities. Traps are primarily observed in depositional environments containing fining upwards sequences, lenses of coarse textured material surrounded by a finer textured sediment, or pods of porous materials surrounded by fine (Rittenhouse., 1972; Szymkiewicz et al., 2011). Other work has suggested dominant trapping produced by interbedding in alluvial environments, crossbedding, and fracturing systems, all acting to limit vertical connectivity of pores (Dunn & Silliman., 2003). In slower hydraulic flow environments characterized by capillary flow, finer sediments become saturated prior to coarser textured materials as a consequence of higher capillary rise (Dunn & Silliman., 2003; Szymkiewicz et al., 2011). This mechanism of trapping is common during slow water table rise events, leading to the generation of a trapped gas pool below a fine sediment.

2.2. Mobilization of gas below the water table

2.2.1. Initiation and transport of non-wetting fluids in the saturated zone

For gas to migrate through a capillary barrier, the buoyant and viscous forces acting to mobilize the gas must overcome the opposing capillary forces that retain the gas in place (Mumford et al., 2009; Pennel et al., 1996; Roy & Smith., 2007). Mobilization of trapped non-wetting fluids can be initiated through several unique mechanisms, acting to exceed the capillary forces that inhibit migration through a saturated porous media. Previous laboratory-based analyses of non-wetting fluid migration through a saturated media have observed mobilization by increasing buoyant forces through expansion (Mumford et al., 2009; Roy & Smith., 2007), increasing viscous forces in a fast-flowing hydraulic regime (Anton & Hilfer., 1999; Moradi et al., 2014), and reducing capillary pressures through surfactant flushing (Chi., 2011; Duffield et al., 2003; Khalladi et al., 2009; Pennell et al., 1996).

Immobile gases generated below the subsurface are comprised of volatile substituents characteristic of the water composition or chemical process in which they were formed (Ronen et al., 1989). In contaminated quasi-saturated groundwater systems, partitioning of volatile chemical constituents to the gaseous phase contribute to the migration and transport of gases through the saturated zone (Mumford et al., 2009; Roy & Smith., 2007). Mass transfer of volatile constituents from contaminated groundwater to gas resulted in an increase in gas pressure of the trapped ganglion. Increases in gas pressure resulted in the expansion of the ganglion, causing migration of gas into connected pores (Figure 2.3). Continuous expansion of trapped gas with volatile partitioning would result in increases in buoyant forces acting to mobilize the gas. Once achieving a critical bubble size, buoyant forces exceed retaining capillary forces, enabling the upward migration of gas through the porous media. A trapped ganglia or non-wetting fluid pool has a representative parameter that demonstrates the relationship between buoyant forces and opposing capillary forces, identified as the Bond number (Pennell et al., 1996):

$$N_{Bo} = \frac{\Delta \rho g k}{\sigma} \tag{2.04}$$

where N_{Bo} is the bond number, $\Delta \rho$ (ML⁻³) is the density difference of the two fluids, g (LT⁻²) is the acceleration due to gravity, k is the permeability of the porous media, and σ (ML⁻²T⁻²) is the interfacial tension at the two-fluid interface. At a critical Bond number, buoyant forces overcome capillary forces, initiating mobilization of a trapped ganglion through a porous medium. If the Bond number is less than this critical value, the ganglion will remain immobile.

The stability of trapped non-wetting fluids is dependent on the hydraulic properties that characterize a flow regime (Moradi et al., 2014). The recovery of trapped crude oil in porous media varies under different hydraulic flow conditions, in which recovery is optimized in faster flow regimes. The viscous forces acting to mobilize a trapped non-wetting fluid are influenced by the hydraulic flow rate of water through a groundwater system. The effects of viscous forces on non-wetting fluid migration trapped by retaining capillary forces can be expressed by the capillary number (Pennell et al., 1996):

$$N_{Ca} = \frac{\mu q}{\sigma} \tag{2.05}$$
where N_{Ca} is the capillary number, q (LT⁻¹) is the Darcy velocity and μ (ML⁻¹T⁻¹) is the viscosity of the aqueous phase. Increases in the hydraulic flow rate result in an increase in the viscous forces acting to mobilize the trapped fluid. After exceeding a critical capillary number, viscous forces overcome capillary forces, leading to the initiation of mobilization of the non-wetting fluid through a porous medium (Moradi et al., 2014).

Modern remediation studies have further investigated the mobilization of trapped residuals in groundwater systems to eliminate contaminant sources from potable aquifers. Surfactant flushing utilizes the dependence of capillary forces on interfacial tension to trigger mobilization by reducing the retaining forces that keep trapped fluids in place (Chi., 2011; Duffield et al., 2003; Khalladi et al., 2009; Pennell et al., 1996). As demonstrated by the Laplace equation of capillarity, capillary pressure is directly proportional to interfacial tension (Equation 2.01). Sorption of chemical surfactants at the interface of two immiscible fluids results in a reduction in capillary pressure proportional to the reduction in interfacial tension induced. Viscous and buoyant forces of an immobile fluid are able to overcome the weakened capillary forces in the presence of a chemical surfactant, causing the mobilization of previously trapped fluids through stratigraphic traps and confining porous media.

2.2.2. Physical mechanisms in gas migration

When the buoyant and viscous forces driving mobilization exceed opposing capillary forces, migration and transport of gas through a saturated system is triggered (Mumford et al., 2009; Roy & Smith., 2007). The critical capillary pressures for fluid transport in a porous media can be quantified in soil retention curves (Figure 2.4; Gerhard & Kueper.,

2003). Entry and terminal pressures defined by the draining and imbibition curve respectively are critical pressures characterizing the migration of fluids in multiphase flow. As the retaining capillary forces are exceeded, displacement of water by gas occurs, in which the capillary pressure characterizing the gas-water interface exceeds the entry pressure of the largest connected pore (Gerhard & Kueper., 2003). This displacement mechanism is characterized as a drainage event, in which gas will only displace water if the capillary pressures of the gas-fluid interface exceeds the critical pressures of advancing pores resisting fluid flow. Gas transport through a porous medium is accompanied by subsequent imbibition, in which water is withdrawn simultaneous to invasion of gas at the smallest pores characterized by the highest terminal pressures (Mumford et al., 2010). The terminal pressure is the minimum critical capillary pressure in which connected non-wetting fluid is no longer sustained upon initiation of imbibition.

For gas migration to be maintained, the capillary pressure in unsaturated pores must continuously exceed the entry pressures resisting mobilization (Roy & Smith., 2007). However, as mobilization continues, reduced buoyant forces resulting from a smaller gas pool limits the capacity to transport gas through the medium. Entrapment of gas is re-established as buoyant forces are no longer able to overcome capillary forces retaining the fluid in place.

2.3. Biofuel gasoline additives and interfacial tension

2.3.1. Types and properties of common biofuel gasoline additives

As fossil fuels account for 80% of primary energy used and consumed by the global population, a need for alternative fuel sources becomes critical as resource availability diminishes with overexploitation (Escobar et al., 2009). The development and advancement of cleaner technologies continues to be a significant area of research in attempt to extend the availability of natural resources and limit the environmental impacts of fossil fuel combustion. The use of biofuels, biodiesels, and biofuel additives become an attractive alternative to crude oil and petroleum-based fuels as global climate concerns arise from continuous emission of vehicular greenhouse gases. Alternative fuels provide an opportunity to limit GHG emissions from combustion engines, and reduce global carbon dioxide concentrations (Elfasakhany., 2014). Application of the plant-based fuel alternatives in vehicles has demonstrated a 48% decrease in GHGs released from car exhaust in experimental analyses, providing promise for use as an alternative. Further work has observed decreases in polycyclic aromatic hydrocarbon (PAH) emissions, hydrocarbon emissions, smoke opacity, and concentrations of soot (Figure 2.5; Rakopoulos et al., 2010; Yang et al., 2016). Being produced from completely natural sources, biofuels, biofuel additives and biodiesels provide a sustainable and renewable alternative to fossil-fuels. The fuels and additives can be synthesized from multiple sources including; palm, sunflower, rapeseed, sugarcane, and many other plant biomass sources, through the process of fermentation, pyrolysis, gasification, and in the cases of

biodiesel, can be used in its raw material form (Escobar et al., 2009; Nigam & Singh., 2011).

The chemical and physical properties of biofuel and biofuel oxygenate additives function to optimize engine combustion, improve combustion efficiency, and reduce emissions in most conventional vehicles (Christensen et al., 2011; Jin et al., 2011; Liu et al., 2016; Yilmaz et al., 2014). Common biofuel additives that are currently being administered, or considered for use, in gasoline and diesel include ethanol (EtOH) and butanol isomers; 1-butanol (1-BuOH), iso-butanol (iso-BuOH), and tertiary-butanol (t-BuOH) (Jin et al., 2011). All these compounds share similar chemical properties, in that they are characterized as amphipathic compounds, with a hydrophobic carbon tail and hydrophilic hydroxyl head (Rosen & Kunjappu., 2012). These chemical moieties facilitate surfactant behaviour, in which the compounds will sorb to an interface between two immiscible fluids. Sorption to an interface results in the alteration of molecule orientation, in which hydrocarbon tails will orient towards the non-polar fluid, and the polar hydroxyl groups will orient towards the polar fluid (Eastoe & Dalton., 2000; Tadros., 2006). Interactions of surfactants at an interface reduces the difference in opposing strengths between the two immiscible fluids, resulting in a reduction in tension across the interface (Rosen & Kunjappu., 2012). The reduction in interfacial tension is a concentration dependent process and is variable with each chemical surfactant. As the concentration of a surfactant at an interface increases, the difference in energies of the opposing fluids decreases, causing a subsequent decrease in a reduction in interfacial tension. This relationship remains until the interface becomes saturated with surfactant,

in which no more sorption sites are available for chemical interaction. Further increases in concentration do not facilitate further reductions in interfacial tension.

2.3.2. Contaminant transport and flow in quasi-saturated systems

In saturated groundwater systems, transport of solutes is dependent on; the hydraulic properties of the system, the chemical and physical properties of the contaminant, and the characteristics of the porous media. Understanding contaminant transport is critical to interpreting the behaviour and fate of biofuel constituents in a flowing groundwater system. The primary processes driving contaminant migration through saturated porous media include advection and hydrodynamic dispersion (Fetter et al., 2017). In saturated systems, solutes are transported along the flow of water through the porous media at the rate of the average linear pore water velocity, defined as the process of advection:

$$\bar{\nu} = \frac{\kappa}{\eta_e} \frac{dh}{dl} \tag{2.06}$$

where \bar{v} (LT⁻¹) represents the average linear pore water velocity, K (LT⁻¹) represents the hydraulic conductivity, η_e is the effective porosity of the porous media, and $\frac{dh}{dl}$ represents the hydraulic gradient. As natural porous media are highly complex and heterogeneous, solutes will travel at rates different from that of the average linear pore water velocity. Variability in the rate of solute transport arises from the rate of fluid transport through a pore, tortuosity present in a porous media, and pore-size variability.

The migration of solutes through saturated media also occurs due to existing concentration gradients, in which contaminants will migrate from high to low concentrations in a fluid (Fetter et al., 2017). The implication of these processes,

identified as mechanical dispersion and chemical diffusion, cannot be differentiated, and are recognized together as hydrodynamic dispersion:

$$D = \alpha v + D^* \tag{2.07}$$

where $D(L^2T^{-1})$ is the hydrodynamic dispersion, $\alpha(L)$ is the dispersivity of the porous media, and $D^*(L^2T^{-1})$ is the effective dispersion coefficient. Hydrodynamic dispersion is quantified along the direction of groundwater flow, as well as the direction transverse to groundwater flow.

The processes of advection and hydrodynamic dispersion can be combined together to model the transport of dissolved solutes through a saturated system, represented by the advection-dispersion equation (Fetter et al., 2017):

$$D_L \frac{\partial^2 c}{\partial x^2} - \bar{\nu}_x \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t}$$
(2.09)

in which C (ML⁻³) is the concentration of aqueous solute, \bar{v} (MT⁻¹) is the average linear pore water velocity, D_L (L²T⁻¹) is the longitudinal dispersion coefficient, x (L) is the depth, and t (T) is time.





Figure 2.1. *Relative hydraulic conductivity as a function of entrapped gas saturation in different porous materials* (Marinas, M., et al. 2013).



Figure 2.2. Distribution of forces acting on an immobile trapped NAPL ganglia in a saturated porous media. The effects of capillary pressure $(2r_n, 2r_p)$ overcoming buoyant forces $(v_o\rho_o g_o)$ on bubble stability in a flowing groundwater system (Pennell, K. D., et al. 1996).



Figure 2.3. *Flow-cell experiments displaying the expansion, migration, and fragmentation of disconnected gas in the presence of TCE*. (a) distribution of gas after 0 days following initial injection, (b) distribution of gas after 2 days following initial injection, distribution of gas after 13.7 days following initial injection (Mumford, K. G., et al. 2009).



Figure 2.4. Capillary pressure-saturation curves, or soil retention curves, and critical characteristic pressures of a multiphase-flow system (Gerhard, J. I., & Kueper, B. H, 2003). P_E represents the entry pressure at a saturation of S_W^M , P_T, represents the terminal pressure at a saturation of S_W^X .



Figure 2.5. Soot density emissions of different concentrations of Butanol relative to diesel fuel under different brake mean effective pressures (Rakopoulos, D. C., et al. 2010). Increased concentrations of biofuel results in reduced soot density.

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Chapter 3: Laboratory experiments investigating the effects of biofuel additives on trapped gas

Abstract

Biofuel additives in gasoline and fuels developed to limit vehicular emissions pose a risk to groundwater systems contaminated by fuel spills and leakages. The chemical nature of biofuel additives facilitates surfactant behaviour in multiphase groundwater systems, having the potential to alter the hydraulic properties that characterize a system. The effects of common biofuel additives on quasi-saturated groundwater zones were analyzed in this work. Laboratory experiments were conducted in a two-dimensional flow cell, containing a capillary barrier heterogeneity that optimized gas entrapment. A gas pool generated below the capillary barrier was contaminated with biofuel additives commonly considered for use in combustion engines. Infiltration of a contaminant spill was established by a generating a downwards hydraulic gradient, in which dissolved additives were transported through the porous medium in a dispersed front with the flow of water. The effects of concentration-dependent interfacial tension on the migration of gas were investigated by analyzing the release of gas through the porous medium, and the associated decrease in pool height over time. Contamination at the top of the gas pool resulted in the initiation of gas migration, resulting in a subsequent decrease in gas pool height with time. Gas migration terminated at a critical pool height proportional to the reduction in interfacial tension induced. Mobilization of gases in quasi-saturated zones will modify the primary hydrogeologic parameters characterizing a groundwater system and is important to consider in gasoline contaminated sites containing biofuel additives.

3.1. Introduction

A complete understanding of the physical behaviours and interactions that take place in groundwater systems and potable aquifers has become a significant focus in scientific literature due to its economic and social relevance as a finite resource. More than ten million Canadians rely on groundwater as their primary water source for consumption and use in; irrigation, farming, and mining (Rutherford., 2004). Monitoring potable groundwater systems for contaminants has become obligatory prior to use as a resource due to its vulnerability to contamination and potential threat to human health (Mackay & Cherry., 1989). As gasoline and fuel spills remain a primary source of contamination below the subsurface, understanding the interactions, fate, and transport of chemical constituents comprising petroleum products in groundwater is crucial for establishing modern mitigation and remediation techniques (Mackay & Cherry., 1989; Corapcioglu & Baehr., 1987). The severe environmental and human health impacts resulting from common gasoline constituents in potable aquifer systems has led to the development of chemical alternatives to fully petroleum-based fuels, that limit adverse effects, while maintaining functionality in vehicles (Suflita & Mormile., 1993).

Previously administered fuel oxygenate-additives, such as, tetraethyl lead (TEL) and methyl tertiary butyl ether (MTBE), detected in potable water sources have been linked to a multitude of acute and chronic illnesses in humans (Hollaender & Storrer., 2014). Biofuel additives are a common alternative to chemical oxygenate additives and octane enhancers, functioning to optimize engine combustion efficiency and octane numbers, while reducing smoke opacity (Yang et al., 2016) and emissions of polycyclic aromatic carbons (PAH), carbon monoxide (CO), benzene, and particulate matter (PM) (Westphal et al., 2010). These additives function as both a renewable and degradable resource, synthesized from biomass, corn, sugar beets, barley and other natural resources (Jin et al., 2011). Bioethanol and biobutanols are the most widely used biofuel additives utilized as modern fuel alternatives and gasoline additives in combustion engines. The unique chemical and physical properties of different biofuel additives influences their performance and efficiency as a fuel additive (Table 3.1).

Ethanol (EtOH) was one of the first fuel-oxygenates developed for use in combustion engines, currently administered as an alternative to fully petroleum-based fuels to replace TEL and MTBE (Al-Hasan., 2003). Many environmental effects of ethanol-based contaminant events have been analyzed to understand the potential consequences of new additives on the natural environment. Although EtOH has been administered to gasoline as an environmentally safe alternative to other additives, recent studies have observed direct effects of EtOH on the degradation and migration of other groundwater contaminants (Alberici et al., 2002; Corseuil et al., 1998; Ma et al., 2013; Schaefer et al., 2010). These studies have demonstrated reduced biodegradation of benzene, toluene, ethylbenzene and xylene (BTEX) in groundwater contaminated with EtOH blended gasoline due to preferential degradation of EtOH causing oxygen depletion for degradation of other compounds (Corseuil et al., 1998; Ma et al., 2013; Schaefer et al., 2010). The presence of EtOH in groundwater systems has also been suggested to enhance the rate of transport of BTEX through enhancing the solubilization of each constituent in water (Alberici et al., 2002; Ma et al., 2013). In addition to the

environmental repercussions of EtOH blended gasoline, EtOH use in vehicles has exhibited poor workability in most engines, in which continuous use of EtOH in internal combustion engines has led to the gradual corrosion and oxidation of engines and metal pipelines (Jin et al., 2011).

The adverse side effects of EtOH use in modern automobiles and groundwater systems has prompted the advancement of biobutanols as an alternative fuel source or fuel additive (Jin et al., 2011). The added complexity of the chemical structure of butanols renders them more soluble in gasoline and diesel fuel blends. Unlike EtOH, butanol additives do not require the addition of chemical surfactants to enhance solubility in oils, improving the manufacturing process by reducing the need for additional cosolvents in fuels. The different isomers of biobutanols have been analyzed for; performance in vehicles as a fuel source, performance in vehicles as an oxygenate additive, renewability and environmental impact. The most common biobutanols considered for use are; 1-Butanol (1-BuOH), iso-butanol (iso-BuOH), and tertiary butanol (t-BuOH).

Use of biofuel additives provides manufacturers a sustainable alternative to crude oils and gasoline in the transportation industry. The simple chemical structure of biofuel additives, characterized by a hydrophilic hydroxyl head and a hydrophobic carbon tail, allows for high performance in vehicles, while facilitating degradation in natural systems. The amphipathic nature of the compounds facilitates surfactant behaviours, in which biofuel additives undergo chemical interactions and sorption at an interface between two immiscible fluids. Chemical interactions with both non-polar and polar compounds that

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comprise the different fluids occur as the molecule orients its non-polar hydrocarbon chain and polar hydroxyl head to the respective fluids (Rosen., & Kunjappu., 2012; Smith & Gillham., 1999). Adsorption of biofuel additives to an interface results in the modification of the interfacial energy of the boundary, defined by Rosen & Kunjappu (2012), as "the minimum work required to create a unit area of interface or expand it by unit area". Reductions in interfacial energy at the boundary, expressed quantitatively as interfacial tension, results upon the sorption of a chemical surfactant to an interface. In multiphase transport and fluid flow in porous media, the effects and behaviours of surfactants at phase boundaries becomes apparent. These effects have been demonstrated in remediation studies using chemical surfactants to mobilize and transport residual NAPLs from groundwater systems (Lee et al., 2005; Pennel et al., 1994; West & Harwell., 1992). By reducing interfacial tension at non-wetting-wetting fluid interfaces at the pore scale, capillary pressure decreases proportionally based on the relationship between interfacial tension and capillary pressure expressed by the Laplace equation of capillarity (Fetter et al., 2017):

$$P_c = \frac{2\sigma}{r} \tag{3.01}$$

where P_c (ML⁻¹T⁻²) is capillary pressure, σ (MT⁻²) is interfacial tension at the nonwetting-wetting fluid interface, and r (L) is the pore radius. The decrease in interfacial tension weakens capillary forces retaining the trapped fluid in place, initiating the migration of non-wetting fluid flow.

Fluid entrapment in the saturated zone has implications on non-wetting fluids trapped in pore spaces below the subsurface, including both NAPLs and air.

Understanding the mechanisms and effects of entrapped gas in quasi-saturated soil systems has become a significant area of research due the capacity in which the phenomena can alter the hydraulic properties of an initially saturated porous medium (Faybishenko., 1995; Marinas et al., 2013; Wang et al., 1998). The changes in hydraulic characteristics have significant implications on hydrogeologic processes including natural infiltration of water (Wang et al., 1998), transport and flow of solutes within soil water (Carter et al., 1959), and industrial water extraction (Yager et al., 2001). Studies analyzing the evolution of trapped gases in a previously saturated system have observed change in hydraulic conductivity, permeability, hydraulic dispersion, and porosity (Marinas et al., 2013; Orlob et al., 1958). The magnitude of change in the hydraulic characteristics is highly variable depending on the volume and distribution of the entrapped gas present in a groundwater system (Marinas et al., 2013). The height of a gas bubble or pool trapped below a capillary barrier can be quantified based on the characteristic capillary pressures defining the boundaries of an immobilized gas (Roy & Smith., 2007):

$$h_{gas} = \frac{P_c^{top} - P_c^{bottom}}{\Delta \rho g}$$
(3.02)

in which h_{gas} (L) is the height of the gas pool, P_c^{top} (ML⁻¹T⁻²) is the capillary pressure at the top of the gas pool, P_c^{bottom} (ML⁻¹T⁻²) is the capillary pressure at the bottom of the gas pool, g (LT⁻²) is the acceleration due to gravity, and $\Delta \rho$ (ML⁻³) is the density difference of air and water.

As gas spills and fuel leakages continue to be a primary source of contamination, it becomes critical to identify and understand the interactions that take place between added fuel constituents with groundwater systems. It is hypothesized, that contamination of an entrapped gas pool with biofuel additives will exhibit mobilization, until terminating at a critical gas pool height quantified by:

$$h_{gas} = \frac{\left(P_c^{top} - P_c^{bottom}\right)\left(\frac{\sigma_{su}}{\sigma_w}\right)}{\Delta\rho g} \tag{3.03}$$

where σ_{su} (MT⁻²) is the interfacial tension of the biofuel surfactant and σ_w (MT⁻²) is the interfacial tension of water. Based on this theory, an immobile gas pool contaminated with biofuel additives will mobilize, such that the reduction in critical pool height will be proportional to the reduction in interfacial tension caused by biofuel additives (Figure 3.1). No studies in the literature have demonstrated the effects of contamination by biofuel additives on the mechanisms of gas migration and termination of gas below the subsurface. Mobilization of gases in quasi-saturated groundwater systems can result in considerable alteration to the primary parameters that define a particular system, having several consequences on monitoring and characterization of different groundwater systems.

The objectives of this work were to 1. investigate the effects of dissolved biofuel additives on the mobilization and migration of trapped gases in quasi-saturated groundwater systems; 2. identify the primary mechanisms driving gas transport in the presence of a chemical surfactant contaminating a gas-fluid interface at the pore-scale, 3. investigate the effects of heterogeneities on the migration of gas through a capillary barrier; 4. investigate the behaviours and distribution of gas in an immobile pool in the presence of an interfacial tension gradient; and 5. demonstrate the effects of an LNAPL

contaminant spill event on the migration and termination of an immobile gas pool trapped below a capillary barrier.

3.2. Methods

3.2.1. *Flow-cell Experiments*

3.2.1.1. Flow cell sand packing

All experiments were conducted using a two-dimensional flow-cell packed with sand in an ideal configuration for air entrapment. The flow-cell apparatus was 58 cm in length and 49.5 cm in height, with a 1.1 cm width between glass plates in order to restrain the system to two-dimensional hydraulic behaviours. Two glass plates were stabilized with a brass support frame, with viton gasket to seal the glass to the brass.

Two simple geometries were constructed in the flow cell for use in different experiments, both packed with a similar capillary barrier geometry (Figure 3.2). A coarse silica sand (Bell & McKenzie GS-20) was used as the background porous medium for the flow regime that surrounded the fine sand (Opta Minerals 56.3.10) capillary barrier heterogeneity. The geometry of the sand pack established a practical and quantifiable model for the behaviour of entrapped gas beneath a fine sand layer heterogeneity, or capillary barrier. Both geometries were constructed using the same procedure, in which dry sand was poured continuously and rapidly for each separate segment (labelled 1 to 9 in the order of pour), to minimize depositional grading and maximize within-layer homogeneity. All sediments were separated by the individual sections in which they were poured and were measured by weight using the Sartorius BP 34000-P scale. Bulk density and porosity estimates were calculated following packing (Table 3.2). A swift pour of sediments was found to be critical for each segment of deposition in order to generate a more uniform and reproducible porous medium. To ensure all sediments measured were deposited into the flow-cell, a custom wooden trough-shaped funnel was fastened to the top of the flow cell to capture all grains during the pouring process (Figure 3.3). Following the pour of each individual sand segment, a mallet was used to vibrate the flow cell to induce settling and compaction, thereby maximizing the bulk density. A small rake was used to slightly disturb the top layer of each sand layer prior to the addition of the next layer to minimize grain orientation heterogeneities at the interface between layers.

All flow cells had a coarser grained sand (Beipecal (B.P) T18.7) layer, deposited to 3 cm in height, at the bottom of the flow-cell to act as a blanket drain which minimized hydraulic head differences relative to the outlet ports on each side of the flow cell. That is, this layer established a constant head boundary at the bottom of the flow regime that would eliminate the influence of the outlet ports on the flow field, inducing predominately vertical flow. Following disturbance and redistribution of grains using the rubber mallet, the second pour was conducted, in which the coarse sand background material, GS-20, was added. The structure of the capillary barrier was outlined using four wooden dowels and temporarily blocked off using felt textiles that were measured to be the same width of the flow cell. The felt textiles functioned to both stabilize the dowels and inhibit deposition of coarse sand in the capillary barrier (Figure 3.3). Segments 3 to 5 were packed individually to create the coarse background. Felt textiles were carefully removed, and the Opta 56 fine sand was poured to fill segments 6 and 7. Once packed,

inner dowels were gently removed to allow for the pour of segment 8. To complete the packing of the coarse background, both outer dowels were removed and GS-20 coarse sand was added to fill segment 9. Once the entire cell was filled, the sand surface was leveled, and complete settling of all grains was encouraged to maximize settling and packing using the rubber mallet.

3.2.1.2. Hydraulic tubing connections

Tygon R-3603 tubing connected to a Y-tubing divider was attached to brass valves on either side of the flow cell (Figure 3.5). A T-joint connector was used to add a segment of tubing, which functioned as a piezometer, and was adhered to a meter stick on the side of the flow cell. This tubing was left open to the atmosphere to allow for accurate pressure head measurements throughout experimentation. The other end of the tubing was secured to a steel retort stand on the other side of the flow cell. With the port valves to the flow cell closed, the tubing was filled with deionized water using a syringe. Air bubbles were removed continuously as they were generated. Once the tubing was placed into a VWR 1000 mL glass beaker filled with water. The amount of water entering the flow cell was measured by mass in the beaker using a Mettler Toledo BD1201 scale. The tubing was secured to a retort stand and suspended in water in order to establish a hydraulic connection between the flow-cell and beaker. The scale and beaker were placed on a scissor jack to allow control of the hydraulic head at all times. 3.2.1.3. Flow cell saturation and gas pool entrapment below fine entrapment layer In order to establish initial wetting conditions in the flow-cell the entire sand pack was saturated with water prior to gas entrapment. Saturating the cell prior to gas entrapment would simulate natural groundwater conditions, such that the gas-water interface of a trapped gas pool would initially exhibit capillary pressures on the respective wetting curves. Saturation of the flow-cell was controlled using a constant head method, in which the water level in the hydraulically connected beaker was raised and lowered to induce saturation and drainage of the sand respectively. This method of saturation would generate entrapped gas through simulating a water table rise event. To increase the hydraulic head, the scissor jack beneath the beaker was raised to a height proportional to the increase in head desired. To inhibit depletion of the water source, hydraulic head was also increased through increasing water level in the beaker by incremental additions of D.I. water. The volume of each addition of water was recorded. All changes in hydraulic head were measured on the piezometer connected to the flow cell.

The flow-cell was initially saturated by raising hydraulic head in 5 to 10 cm increments every 2 minutes until a minimum of 3 cm of water ponded the sand surface. This rapid saturation mechanism minimized gas entrapment below the fine entrapment layer during this stage, allowing near complete saturation of the entire sand pack. The flow cell was covered and left to sit for a minimum of 12 hours to establish equilibrated conditions.

Once equilibrated, the sand was drained of water by lowering the scissor jack and removing volumes of water from the beaker, inducing an incremental decrease in hydraulic head. Once drained, the gas entrapment process could begin. Hydraulic head was increased at a slower rate than the initial saturation, in 2 to 3 cm increments every 5 to 10 minutes, in order to minimize the generation of gas in the coarse background material. The hydraulic head was increased until the capillary fringe of the coarse material had just surpassed the bottom of the capillary barrier arms, labelled 6 and 7 of fine material (Figure 3.2). The flow cell was covered and left to sit for a minimum of 12 hours to not only encourage dissolution of small gas residuals, but also to promote saturation of the fine sand confining layer. The contrasting material properties of the fine and coarse sand materials used was enough to exhibit considerably different capillary fringe heights upon gradual saturation. Since the height of capillary rise is inversely proportional to the size of the pore radii, capillary rise of the fine material exceeds that of the coarse sand (Equation 3.06).

$$h = \left(\frac{2\sigma}{r\rho g}\right)\cos\theta \tag{3.06}$$

where h (L) is the height of capillary rise, σ (MT⁻²) is the interfacial tension of the airwater interface, r(L) is the pore radii, ρ (ML⁻³) is the density of water, g (LT⁻²) is the acceleration of gravity, and θ is the apparent contact angle (Fetter et al., 2017). This mechanism allows for complete saturation of the fine entrapment layer by capillary rise prior to saturation of the coarse sand, closing off the air in the capillary barrier from connection to the atmosphere. Once the confining layer was completely saturated, the hydraulic head was raised to saturate the rest of the flow-cell, coarse background material. The hydraulic head was raised slowly, 2 to 3 cm every 5 to 10 minutes until the coarse material was saturated and a minimum of 3 cm of water had ponded the surface of the sand pack. The height of the gas pool trapped beneath the fine entrapment layer was measured prior to contamination (Table 3.4).

3.2.1.4. Contamination of aqueous phase biofuel alcohols through continuous infiltration: constant head method

All surfactants were prepared in 2-litre volumes based on the particular chemical properties of each chemical in order to produce an aqueous solution of each prior to experimentation. As EtOH is 100% miscible in water, no prior dilution was required. However, t-BuOH and iso-BuOH were diluted to produce an aqueous solution for infiltration (Table 3.4). Iso-BuOH was diluted to its solubility in water to inhibit free phase NAPL from contaminating the system. Similarly, t-BuOH was diluted to 50% w/w. Although t-BuOH is 100% miscible in water, the chemical exists as a solid phase at room temperature. To inhibit solid formation in the flow cell and obstruction of pore sites by freezing, the chemical was diluted. This concentration was selected as an appropriate dilution as precipitation would be inhibited due to the high solubility of t-BuOH in water, in addition to the fact that any further increase in concentration does not cause considerable reductions in interfacial tension. Each aqueous surfactant experiment was performed in duplicate on the flow-cell packing arrangement number 1 (Figure 3.2.a).

Infiltration of each individual surfactant was induced using a constant head method (Figure 3.5). A 500 mL VWR glass beaker containing 250 to 300 mL of aqueous surfactant was elevated to the height of the water table in the flow cell using a scissor jack. A 20 cm long Tygon R-3603 tube (1.3 cm inner diameter) hydraulically connected the surfactant input beaker to the flow-cell in order to generate a siphon system. The

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cross-sectional area of one tubing end was reduced through the use of a medical grade mesh and was submerged into the ponded water above the sand pack. The fluid in the beaker was levelled to the height of the ponded water in the flow cell using a bubble level to ensure no fluid transfer would occur prematurely. With the flow valves closed, the height of the tubing connected to the base of the flow-cell was lowered below the water table to function as the discharge outlet, and was gently clamped to a steel retort stand to maintain its height during the experiment. An empty 1000 mL VWR glass beaker placed on the Mettler Toledo PG5002-S Delta Range scale was kept below the outlet tube to continuously measure discharge.

To initiate contaminant transport through the flow-cell, the flow valves at the bottom of the flow-cell were opened (Table 3.4). The clean water ponded along the surface of the sand was displaced with aqueous surfactant introduced through the siphon system. Once ponded to establish a maximum concentration boundary along the top of the porous medium, infiltration was initiated. Infiltration was induced by creating a downwards flux through the sand pack by lowering the height of the discharge, outlet tube to 2 ± 1 cm below the ponded water surface. The ponded water was maintained at a constant elevation through 25 mL additions of surfactant to the siphon beaker. Measurements of the volume of surfactant added, discharge mass, hydraulic head of outlet, and elevation of water table, were recorded every minute throughout the experiment. Advective transport of the aqueous surfactant through the flow-cell was computed as a first approximation to contaminant arrival at the upper boundary of the gas pool, as the dissolved aqueous biofuel additive fronts were not visible in all experiments.

Using the volume of surfactant added, the flux of contaminant migrating through the flow cell was computed based on Equation 3.07:

$$x = H_s - \left(\frac{V_{add} - V_{pool}}{(A)\eta}\right) \frac{\rho_{su}}{\rho_w}$$
(3.07)

where x (L) is the depth of contaminant in flow-cell, H_s (L) is the height of the sand pack, V_{add} (L³) is the volume of surfactant added to the flow-cell, V_{pool} (L³) is the volume of the pool above the sand pack, A (L²) is the cross-sectional area of the flow-cell column, η is the porosity of the porous medium, ρ_{su} (ML⁻³) is the density of the biofuel surfactant, and ρ_w (ML⁻³) is the density of water. Video recordings of the experiments were conducted using the Sony HDR-CX405 flash memory camcorder and analyzed for gas pool height and gas transport behaviours in one-minute intervals using Monosnap 4.1.4 editor. To analyze the gas pool height relationship to interfacial tension reductions, the contaminated pool height ratio was computed based on the final measured pool height to the initial:

$$H_{F:I} = \frac{H_{Co}}{H_0}$$
(3.08)

where $H_{F:I}$ is the ratio of the final pool height to the initial generated gas pool height, H_{Co} (L) is the height of the gas pool after complete contamination with surfactant, and H_{θ} (L) is the initial height of the gas pool before contamination with surfactant.

3.2.1.5. Contamination of LNAPL at constant pool depth

In order to analyze the behaviour of a three-phase system and the associated effects on entrapped air mobilization, pure 1-BuOH was selected as a representative biofuel LNAPL for use in contaminating the flow-cell. All 1-BuOH experiments were conducted on the flow-cell packing arrangement number 2 (Figure 3.2b) to optimize experimental time. Contamination was initiated similar to the aqueous surfactant experiments, however, the pure LNAPL pool was lowered and maintained at a near constant elevation in the sand pack to establish a maximum concentration boundary. Similar to contamination with aqueous surfactants, hydraulic head measurements were recorded every minute using the connected piezometer, along with continuous measurements of water level height. Mass balance measurements were also conducted in which the volume of 1-BuOH added and discharge mass were taken every minute.

Contaminant transport was calculated as a first approximation based on analysis of the visible aqueous 1-BuOH front, by measuring the apparent rate of transport through the flow-cell. The LNAPL front was visualized as a darker coloured region of the porous medium. Contaminant breakthrough curves of aqueous 1-BuOH were computed using the one-dimensional advection-dispersion equation based on the measured variables (Fetter et al., 1999):

$$D_L \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t}$$
(3.09)

in which C (ML⁻³) is the concentration of aqueous 1-BuOH, (MT⁻¹) is the average linear pore water velocity, D_L is the longitudinal dispersion coefficient, x (L) is the depth, and t(T) is time. The one-dimensional Ogata-Banks analytical solution was used to solve the differential equation using experimental boundary conditions to simulate the transport of the aqueous 1-BuOH front overtime:

$$C = 0.5C_0 \left[erfc \left(\frac{L - \bar{v}t}{2\sqrt{D_L t}} \right) - e^{\left(\frac{\bar{v}L}{D_L} \right)} erfc \left(\frac{L + \bar{v}t}{2\sqrt{D_L t}} \right) \right]$$
(3.10)

where C_{θ} (ML⁻³) is the initial concentration of aqueous 1-BuOH and L (L) is the distance of transport for the average particle. Interfacial tension was calculated after determining the concentration of 1-BuOH at the upper boundary of the gas pool overtime based on a concentration dependent interfacial tension relationship for 1-BuOH derived by Smith & Gillham., 1999:

$$\sigma = \sigma_w \left(1 - b \left(\ln \left(\frac{C_{BuOH}}{a} + 1 \right) \right) \right)$$
(3.11)

Where σ_w (MT⁻²) is the interfacial tension of water, and *a* and *b* are parametric constants specific to 1-BuOH determined to be 0.00365 and 0.215 respectively.

3.2.1.6. Contaminant drainage and sand pack rinsing: saturated and unsaturated flush

To reduce variability in experimental results due to new heterogeneities and differences in sand packing arrangement, the flow-cell packing was conducted once and thoroughly rinsed following each contamination experiment. To ensure all contamination was removed from the flow cell, the saturated sand pack was flushed with a minimum of 7 pore volumes of D.I. water. The Mandel Scientific Minipuls 3 peristaltic pump was connected to the top of the flow cell and submerged in the ponded solution at the surface of the flow-cell (Figure 3.6.a). With the flow valves initially closed, the outlet tubes were hydraulically connected to a large volume of water elevated above the water table in the flow cell using a scissor jack. This elevation would induce an upwards hydraulic gradient through the sand pack in order to flush low density fluids out of the porous medium. Upon opening the flow valves, water was introduced through the bottom ports and discharged through the top of the cell at a constant discharge rate (Q) of 24.8 mL·min⁻¹ controlled by the peristaltic pump. As the water level in the input container decreased, the scissor jack was raised to prevent a reversal of the upwards hydraulic gradient.

Following the saturated flush, the flow cell was drained by incrementally decreasing hydraulic head, as performed during the gas entrapment process. The flow cell was covered and left for a minimum of 12 hours to maximize drainage. As the fine entrapment layer exhibits higher water retention than the coarse background material, contaminated water likely remained in available pores or pore walls of the fine sand following drainage (Brady & Weil., 2010). To ensure this layer was cleaned of surfactant, an unsaturated flush was conducted. A minimum of 1-litre of D.I. water was introduced through the top of the dry sand surface using a syringe in 60 mL intervals. Water preferentially saturated the fine material, allowing for an isolated flush of the capillary barrier (Figure 3.6.b). After the initial unsaturated flush, the cell was completely saturated, covered, and left for a minimum of 12 hours to promote partitioning of remaining chemical constituents to the clean water. The drainage and unsaturated flush were repeated once more prior to the air entrapment process for the consecutive experiment.

3.2.2. Measurement of soil water retention curves using the Hanging Water Column method

3.2.2.1. Sand packing and column set-up

The soil hydraulic properties for Opta 56.3.10 and GS-20 were characterized using the hanging water column method for both samples. The apparatus was assembled using a Pyrex 350 mL glass Buchner funnel with a ceramic porous plate (Figure 3.4). The Buchner funnel was connected to Tygon R-3603 (1.3 cm inner diameter) tubing and clamped and stabilized less than one meter above the lab bench to a steel retort stand.

The tubing was connected to a 100 mL glass burette, stabilized with two three-prong extension clamps to the retort stand. Sand was weighed and added to the Buchner funnel in one quick pour to minimize heterogeneities and depositional grading throughout the column (Table 3.3). Soil properties such as bulk density and porosity were computed using equation 3.04 and 3.05 respectively:

$$\rho_b = \frac{m_T}{v_T} \tag{3.04}$$

$$\eta = \left(1 - \frac{\rho_b}{\rho_s}\right) 100\% \tag{3.05}$$

where ρ_b (ML⁻³) is the bulk density of the sample, m_T (M) is the total mass of the sample, V_T (L³) is the total volume of the sample, η is the porosity, and ρ_s (ML⁻³) is the density of soil solid, assumed to be 2.65 g·cm⁻³.

The column was designed to be 3 cm in height to allow room for ponding water and qualitative observation of the sand surface. Once the sand was poured, the surface of the column was compacted, and the surface grains were gently raked. The funnel was sealed with parafilm to minimize evaporation and punctured to open the system to the atmosphere. A meter stick was adhered to the retort stand where 0 cm was aligned with the surface of the column using a bubble level for capillary pressure head measurements.

Once the hanging water column was assembled with the soil column, 20 mL of a 0.3% bleach-water solution was flushed through the porous cup and sand column to function as a biocide, inhibiting microbial growth throughout the duration of the experiment. The column was then rinsed with three pore volumes of deionized water to remove the bleach solution and clean the sand of possible residuals. Once rinsed, the

column was prepared for measurements by saturating the sand to establish initial wetting conditions.

3.2.2.2. Hanging water column

Using the hanging water column method, the soil water retention *drainage* curve was generated initially. The water level in the burette was aligned with the surface of the sand column using a bubble level, with the burette valve closed. The drainage process was initiated upon lowering the burette to 1.0 cm below the column surface and opening the burette valve to induce a decrease in pressure head. Once lowered, the system was left to achieve an equilibrium capillary pressure, in which water would no longer be drained from the column. Equilibrium was identified as no further change in water volume or water level at the designated capillary pressure. Measurements of water volume and water level height in the burette were recorded in a minimum of 30-minute intervals to ensure the equilibrium capillary pressure was achieved. The volumes of water drained from the burette were converted to volumetric water content based on:

$$\theta_w = \frac{V_{sw} - \Delta V_w}{V_T} \tag{3.12}$$

where θ_w is the volumetric water content, V_{sw} (L³) is the volume of water in the sample when fully saturated ΔV_w (L³) is the change in the water volume in the burette, and V_T (L³) is the total volume of the sample. Volumetric water content was converted to saturation for the generation of capillary pressure-saturation curves (P_c-S) defined as:

$$S_w = \frac{\theta_w - \theta_{rw}}{\theta_{sw} - \theta_{rw}} \tag{3.13}$$

where S_w is water saturation, θ_{sw} is the saturated volumetric water content, and θ_{rw} is the residual volumetric water content.

Once drainage at the applied pressure change was complete, the burette valve was closed, and the burette was lowered 0.5 cm. The valve was then opened again, and the column was left to achieve equilibrium conditions, recording measurements in a minimum of 30-minute intervals. This process was repeated in 0.5 cm intervals to ensure the inflection point of the drainage curve was captured. Once the drainage curve had reached residual saturation and any further increase in capillary pressure induced no change in water volume released from the column, the drainage process was deemed complete.

To measure the wetting curve, the burette was raised in 0.5 cm intervals, and measurements were collected in a minimum of 30-minute intervals until equilibrium conditions were achieved. This process was repeated until an increase in pressure head would no longer induce any further change in water volume entering the column.

All data collected was input into the RETC computer code to generate the soil retention curves and the associated hydraulic parameters of the soil samples (Van Genuchten, M. T., et al. 1991). The data were fit to the Brooks-Corey parametric model:

$$\left(\frac{P_c}{P_d}\right)^{-\lambda} = \frac{(S_w - S_{wr})}{(1 - S_{wr})} \tag{3.14}$$

where $P_c(L)$ is capillary pressure expressed as an equivalent height of water, $P_d(L)$ is the displacement pressure of the material, $S_w(-)$ is the saturation of wetting fluid, $S_{wr}(-)$ is the residual saturation of wetting fluid, and $\lambda(-)$ is a parameter representing the pore-size distribution of the medium.

3.3. Results and discussion

3.3.1. Sediment characterization and hydraulic properties

The sediments used in all flow cell experiments were quantified through the generation of capillary pressure-saturation curves, or P_c-S curves. These curves provide a conceptual representation of the pore-size distribution of a representative elementary volume, as well as provide insight on several soil hydraulic properties useful for modelling and soil characterization (Gerhard & Kueper., 2003). Critical capillary entry and terminal pressures influencing multiphase flow phenomena were quantified using the Pc-S curves. The P_c-S curves for drainage and imbibition were generated for each sediment type used in all experiments (Figure 3.7; Figure 3.8). The different sediment types displayed behaviours characteristic of a well-sorted, coarse sand (GS-20), and a poorly sorted, fine sand (Opta-56). The slope and separation of the imbibition and drainage curves of the GS-20 sand is both steeper and closer together than the Opta-56 sand (Fetter et al., 2017). The sharp slope of the drainage curve of the GS-20 material indicates that upon initiation of desaturation, small incremental increases in capillary pressure would induce drainage from the majority of the pores comprising the material (Figure 3.7). A similar trend was displayed in the GS-20 imbibition curve, in which once the material began to re-saturate, small decreases in capillary pressure would cause a considerable quantity of the pores in the material to fill with water. These findings indicate that the GS-20 coarse sand is a uniform material, characterized by a smaller grain size distribution with a narrow grain size range. In contrast, the Opta-56 P_c -S curves displayed greater separation between the drainage and imbibition curves, both with a shallower slope (Figure 3.8). These graphical

features are characteristic of a larger pore-size distribution, in which a wider range of grain sizes comprises this sand. Small changes in capillary pressure result in a smaller change in saturation. Upon initiation of desaturation, a small increase in capillary pressure would only drain the largest pores in the material. Further increases in capillary pressure would drain smaller pores, however, the decrease in saturation would be minimal. The increase in capillary pressure required to induce complete desaturation is much greater than the well sorted, GS-20 sand, as drainage from smaller pores require much higher suction.

The critical pressures that characterize the multiphase flow behaviours of each porous medium were quantified using the Brooks-Corey model generated using the data fitting software, RETC (Table 3.5; Figure 3.7; Figure 3.8). The model allowed quantification of the entry and terminal pressures of each material by identifying the inflection points of the drainage and imbibition curves respectively. These critical pressures provide further quantification of the sediment properties and pore size distribution of the materials. The entry pressure of the GS-20 sand was 10.36 cm, while the entry pressure of the Opta-56 sand was 20.92. The finer sand required a much higher capillary pressure to initiate drainage from the largest pores in the medium, expressing a considerable difference in pore size between the two materials. During column wetting, saturation of the pore space would terminate at a residual saturation corresponding to the terminal pressure, measured to be 4.70 cm in the GS-20 sand and 12.80 cm in the Opta-56 sand. At this pressure, no non-wetting fluid (air) is connected, and trapped residuals prevent complete water saturation (Gerhard & Kueper., 2003). As trapped non-wetting
fluids tend to occupy the largest pores in a material, further increases in capillary pressure past the terminal pressure results in no further decrease in saturation (Orlob & Radhakrishna., 1958).

It is apparent in Figure 3.7 and Figure 3.8 that the hysteretic behaviours differ between the porous materials GS-20 and Opta-56. Qualitative analysis of the P_c-S curves displays a wider curve separation between wetting and draining of the column in the Opta-56 sand than the GS-20 sand. This behaviour can also be quantified by the P_t:P_c ratio of the materials, in which the ratio for the Opta-56 sand was 0.58 and the ratio for the GS-20 sand was 0.46 (Gerhard & Kueper., 2003). The difference in hysteretic behaviours of the two materials suggest variability in the pore structures of the sands. The most critical parameter controlling the hysteresis of a porous media is its aspect ratio (Dey et al., 2017; Jerauld & Salter., 1990). As the pore throat radii is the primary variable controlling the ability to drain pores, and the pore body radii is the primary variable controlling the ability to saturate pores, the ratio of pore throat size to pore body size dictates the hysteretic behaviour of a porous medium. A material with a wider pore size distribution will display greater variability in the difference in size between pore throats to pore bodies, leading to more hysteresis, as observed in the Opta-56 sands.

3.3.2. Generation of a trapped gas pool in response to water table fluctuations

The gas pool heights generated for each experiment were measured prior to contamination to provide insight on the initial conditions of the trapped air (Table 3.4). The average gas pool height generated for the experiments conducted on packing arrangement 1 for analysis of contamination of aqueous biofuel surfactants was

7.7±0.4cm. Despite effective gas pool reproducibility between experiments, the average height was less than the theoretical height expected based on the P_c-S curve critical capillary pressures and Equation 3.02. As the entrapped gas was created by simulating water table fluctuations in an initially saturated porous media, the initial capillary pressures of the gas-water interfaces applied to Equation 3.02 were assumed to equate the terminal pressures of the respective materials. Since the gas pool was generated in an initially saturated porous medium, with water-wet solids, it was expected that the boundaries of the gas pool initially existed on the wetting curves of the respective porous materials prior to contamination with biofuel additives. In other words, the theoretical gas pool height was expected to be 8.2 cm based on the assumption that the capillary pressure at the top of the gas pool was equal to the terminal pressure of the Opta-56 sand, and the capillary pressure at the bottom of the pool was equal to the terminal pressure of the GS-20 sand. This difference between the theoretical and measured initial gas pool heights captures the variability in sediment packing arrangement and hysteresis of the materials. The theoretical trapping height of the gas pool is based on a macroscopic approximation of representative pore scale characteristics and assumes the pressures are continuous along the interface without variability in sediment arrangement (Szymkiewicz et al., 2011). If the pores at the boundaries of the gas pool existed at capillary pressures on a scanning curve, or exist at a saturation between completely drained or filled, the gas pool height may differ from the initial assumption. Similarly, this variance may result if the upper boundary of the gas pool was not perfectly defined. Variability in pore size distribution and water retention properties along the bottom of the capillary barrier may

induce some gas migration and redistribution into the fine material and would be qualitatively expressed as a slightly smaller visible pool.

The average gas pool height established in packing arrangement 2 for analysis of 1-BuOH contamination was 8.2±0.4cm. The trapped gas pools in this packing arrangement supports the theoretical gas pool height of 8.2 cm that assumes both sediment materials exhibit initial wetting conditions, where capillary pressures at the boundaries of the gas pool were equated to the respective terminal pressures of each material. Agreement of the experimental measured pool height with the theoretical gas pool provides insight on the initial conditions of the porous medium and capillary pressures defining air-water interfaces of the immobile air. Prior to contamination, the capillary pressures at the upper boundary of the gas pool may be represented by the terminal pressures of the Opta-56 sand, while the capillary pressure at the bottom of the pool are defined as the terminal pressures of the GS-20 sand. The terminal pressures of both materials may represent the average pore characteristics along the pool boundaries, and not each individual pore. The capillary forces of the Opta-56 capillary barrier acted to retain the air in place through overcoming the opposing buoyant forces of the gas pool. As a result, air is unable to displace water in pores of the fine material prior to contamination with a chemical surfactant, resulting in the immobility and trapping of a gas pool.

3.3.3. *Migration and termination of immobile gas contaminated with aqueous surfactant*

Contamination of the quasi-saturated system with aqueous iso-BuOH and EtOH through advective-dispersive transport within the porous medium induced the mobilization of entrapped gas through the confining capillary barrier (Figure 3.9). Continuous infiltration of these aqueous surfactants through the flow-cell resulted in the release of gas through the capillary barrier observed as intermittent continual bubbling into the water ponded on the surface of the sand in the flow-cell, accompanied by a corresponding decrease in height (thickness) of the entrapped gas pool with time (Figure 3.9.a-c). Mobilization of gas was initiated as the upper boundary of the gas pool became contaminated with surfactant. The mobilization was observed as a single release pathway, or finger, extending through the capillary barrier, and the coarse sand above, to the surface of the flow-cell. As the concentration of the chemical surfactant increases over time at the upper boundary of the gas pool, the interfacial tensions of the pore scale gas-fluid interfaces decrease non-linearly (Figure 3.1). Reduced interfacial tensions at the upper boundary of the gas pool cause a proportional decrease in capillary pressures at that location in the porous medium (Equation 3.01). It was assumed during analysis that the applied surfactants did not induce significant changes in surficial wettability properties of the solid phase. However, it is recognized that contact angle effects could contribute to the capillary pressure dynamics, but could not be isolated or directly quantified in this work. Reduction in capillary pressures, and thus entry pressures, initiated gas invasion through the capillary barrier at the largest connected pore available for invasion of gas.

Gas invasion continued through the capillary barrier in a series of connected pores favourable for gas flow which was observed as a visible gas finger.

Despite similar behaviours, mobilization was initiated at different times between ExpI1(100 minutes), ExpI2 (40 minutes) and ExpE2 (44 minutes) (Figure 3.9.d). Mobilization of a trapped gas pool contaminated with aqueous EtOH in ExpE2 was initiated as the approximate advective front arrived at the top of the capillary barrier. At this time, the aqueous EtOH front was also qualitatively observed at the top of the capillary barrier, visible as a darker coloured-sharp front. As mobilization was initiated prior to the arrival of the advective front, low concentrations of aqueous EtOH transported by hydrodynamic dispersion were enough to reduce interfacial tension and trigger gas flow. Breakthrough of gas at lower surfactant concentrations suggests interfacial tension reductions required to overcome the largest entry pressures of proceeding pores were minimal.

Gas invasion would continue through the capillary barrier in a series of connected pores favourable for gas flow, observed as gas fingers visible as light coloured, unsaturated pores. If smaller pores characterized by higher entry pressures occupy the upper boundary of the gas pool, larger reductions in interfacial tension would be needed to reduce capillary pressures enough to trigger gas flow. These effects were observed when an immobile gas pool was contaminated with aqueous iso-BuOH in ExpI1 and ExpI2 (Figure 3.9.d). In both ExpI1 and ExpI2, the approximate advective front had reached the upper boundary of the gas, after 85 minutes and 40 minutes respectively. This would suggest that the largest connected pore in the capillary barrier available for gas invasion in both experiments required larger reductions in entry pressure to trigger gas flow. Differences in the rate of contaminant migration was a direct result of different applied hydraulic gradients, summarized in Table 3.4. For ExpI1, initiation of gas migration was observed through a connected finger through the outer edge the capillary barrier (Figure 3.10). Sediment redistribution and/or rewetted saturation conditions may have occurred between experiments, causing small variability in the flow-cell sand pack. That is, redistribution and disturbance of sediments may have resulted from previous mobilization events and/or during flow-cell flushing following each experiment, and/or during rewetting of the flow-cell at the beginning of each experiment. Gas migration through the porous medium is highly sensitive to variabilities in the pressure distribution across the capillary barrier and would vary with changes in pore distribution and water retention properties.

Gas release was sustained as the aqueous surfactant front continued to migrate through the flow-cell, corresponding as a decrease in gas pool height with time (Figure 3.9.d). After 50% of the entrapped gas was released, the gas pool height had decreased as an easily observed sharp front to heights of 5.0 ± 0.3 cm (ExpI1), 5.2 ± 0.3 cm (ExpI1), and 4.5 ± 0.3 cm (ExpE1) that extended the full width of the coarse material below the finer capillary barrier (Figure 3.9.b). In all experiments, the gas was transported as discrete episodic escape events through several finger paths through the capillary barrier as gas fragmented and migrated through the porous medium. Fingers would be generated at connected sites most favourable for gas invasion into pores with the lowest entry pressures, which became visible as lighter coloured connected paths of unsaturated

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porous medium (Figure 3.11). Gas migration through the flow-cell becomes more favourable at shallower depths in the porous medium, as interfaces encounter higher concentrations of surfactant with lower interfacial tensions and additionally lower hydrostatic pressures. Advancement of the contaminant front through the flow-cell generated more gas release paths as the interfacial tensions at the upper boundary of the gas pool were reduced further over time. Higher concentrations and reduced interfacial tension at the upper boundary further reduced entry pressures at the top of the pool with time, thereby contributing to sustaining gas migration through the capillary barrier. That is, smaller pores with higher entry pressures that were not previously available for gas invasion became available for gas flow as interfacial tensions decreased and associated entry pressures were reduced. New finger pathways were thereby generated at smaller pore sites, facilitating the escape of gas through the capillary barrier through multiple pathways as demonstrated in ExpE1(Figure 3.11). Gas release was observed through similar fingers in the same locations in most experiments, as new gas release paths opened up as contaminant infiltration progressed.

Gas flow through the capillary barrier terminated in all experiments at a reduced gas pool height as the contaminant front had reached the bottom of the gas pool (Figure 3.9.c). The final measured gas pool heights were 3.4 ± 0.2 cm (ExpI1), 2.6 ± 0.2 cm (ExpI2), and 2.8 ± 0.4 cm (ExpE1) after termination of gas flow. Since the concentration-dependent interfacial tension is non-linear, additional interfacial tension decreases with concentration are lower at higher surfactant concentrations (Figure 3.1). As a result, entry pressures along the upper boundary of the gas pool were no longer able to facilitate gas

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flow from the smaller gas pool despite the arrival of higher surfactant concentrations with time. Gas terminated at a critical pool height in experiments characteristic of the capillary pressures of the contaminated system. The reduction in gas pool height after complete contamination was proportional to the reduction in interfacial tension induced at the boundaries of the gas pool (Table 3.6).

The contaminated pool height ratio of the final contaminated pool height divided by the initial gas pool can be directly related to the ratio of the EtOH/iso-BuOH-gas to water-gas interfacial tension of 0.31. The contaminated pool height ratio measured in ExpI2 was 0.34+0.04 and in ExpE1 was 0.37+0.07. The theoretical gas pool height of the contaminated system based on the initial generated gas pool using Equation 3.03 was expected to be 2.4 cm for all experiments. This was supported by ExpE1 and ExpI2. However, the final gas pool measured in ExpI1 was larger than ExpI2 and ExpE1, with a contaminated pool height ratio of 0.46+0.05. Theoretical final pool heights were computed using Equation 3.03 with the assumption that the capillary pressures at the top and bottom of the gas pool were initially equal to the terminal pressures of the respective porous material types (Table 3.7). The theoretical final pool height when contaminated with iso-BuOH, assuming initial wetting conditions, was calculated to be 3.2 cm, similar to the final pool height measured in ExpI1 of 3.4 ± 0.2 cm (Figure 3.9.c). If the saturation of pores at the lower boundary of the gas pool existed on a scanning curve (Figure 3.7; Figure 3.8), exhibiting capillary pressures between the entry and terminal pressures characteristic of the GS-20 sand, a smaller final gas pool height would be expected to be established. As the theoretical pool height calculations are based on locally averaged

capillary pressures at the upper and lower boundary of the gas, variabilities and irregularities in the local pore saturation or pore structure are not explicitly accounted for. The small differences in pore distribution and water retention properties between experiments could impact migration pathways, as well as snap-off mechanisms, in which unique terminal pool heights reflect pore-scale variability.

3.3.4. Mechanisms driving gas migration and termination

The stability of an immobile gas pool is dictated by the balance of forces acting on the gas. Flow of gas through a porous medium is initiated when the buoyant forces of the gas overcomes the capillary forces that retain the pool in place. In a flow regime characterized by low hydraulic flow rates, the effects of viscous forces are minimal. In all aqueous transport experiments, buoyant forces were the primary driver of gas flow through the porous medium, as bond number always exceeded capillary number (Table 3.8). Contamination of pore interfaces at the upper boundary of the gas pool by a chemical surfactant causes a reduction in capillary forces that act to inhibit gas flow. Weakened capillary forces can be exceeded by buoyant forces of the gas pool, allowing gas migration through the porous medium. As gas displaces water in proceeding pores in the capillary barrier, water must displace gas in the pool simultaneously. Imbibition occurs at the bottom of the pool at the smallest pores with the highest terminal pressures most favourable for withdrawing water. The simultaneous imbibition of water during gas transport through the porous medium was observed experimentally as a decrease in gas pool height with time, as discussed previously.

For gas transport to be sustained, buoyant forces of the gas pool must continuously exceed capillary forces. During gas flow through the capillary barrier, gas release was discontinuous, temporarily terminating at a reduced gas pool height (Figure 3.12). When the immobile gas pool was contaminated with iso-BuOH in ExpI1, brief termination events were observed over time displayed as periods of constant pool height, that did not last for longer than 5 minutes. Termination of flow was observed at 122 and 130 minutes. Termination of gas flow was observed over longer time periods in other experiments. In ExpI2, migration was terminated temporarily after 67 minutes at a pool height of 5.9 cm+0.4 cm. Similar termination was observed in EtOH and t-BuOH experiments at a gas pool height of 3.5 ± 0.3 cm after 71 minutes (ExpE1), 1.1 ± 0.2 cm after 136 minutes (ExpT1) and 1.8±0.2 cm after 124 minutes (ExpT2). After brief termination events, remobilization was initiated again as interfacial tension at the upper boundary of the gas was further reduced over time. Thereby, gas flow through the porous medium in all experiments occurred episodically as fragmentation of flow disconnected gas fingers from the pool. If pores were available for gas invasion, mobilization would be initiated again. However, if the weakened capillary forces of the contaminated capillary barrier could not be exceeded by the buoyant forces of the gas pool, migration would terminate temporarily. For gas to remobilize again, higher concentrations were required to further reduce entry pressures of the fine sand and open up new migratory pathways for gas transport of a smaller, contaminated gas pool. Advancement of the contaminant front at higher concentrations generated more pathways available for gas flow through smaller pores that were previously unfavourable for gas invasion. During the times in which gas

flow was terminated, an increase in discharge of water out of the flow-cell was observed (Figure 3.13). An increase in discharge rate from $7x10^{-7}$ m·s⁻¹ to $1x10^{-6}$ m·s⁻¹ at 67 minutes was observed when gas flow was terminated in ExpI2, from $4x10^{-7}$ m·s⁻¹ to $1x10^{-6}$ m·s⁻¹ at 71 minutes in ExpE2, from $2x10^{-7}$ m·s⁻¹ to $4x10^{-7}$ m·s⁻¹ at 136 minutes in ExpT1 and from $9x10^{-8}$ m·s⁻¹ to $2x10^{-7}$ m·s⁻¹ at 124 minutes in ExpT2. Other fluctuations in discharge were a result of variability in manual applied hydraulic gradient due to small fluctuations in induced water table height with time. Overall, these trends demonstrate the effects of imbibition during gas migration. During mobilization of gas, discharge of fluid to the outlet ports was reduced considerably, as water went into storage (was withdrawn) to displace the mobilized gas. However, termination of gas migration resulted in a slight increase in discharge as water no longer contributed to displacement of gas, migrating with the hydraulic gradient through the flow-cell.

Indefinite termination of gas transport in experiments at critical pool heights, as discussed previously, occurred as a result of two primary mechanisms. The first mechanism is a direct result of reduced buoyant forces of a smaller gas volume trapped beneath the capillary barrier. As gas pool height decreased with time, the buoyant forces driving mobilization were reduced, and were unable to overcome the capillary forces of the contaminated capillary barrier. For further migration of gas to occur, interfacial tension, and thus capillary pressures, comprising the capillary barrier must be reduced to facilitate gas invasion at favourable pore sites. However, as interfacial tension decreases non-linearly with concentration, further transport of aqueous surfactants through the flow-cell does not facilitate gas flow. The second mechanism is caused from limited

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imbibition at the lower boundary of the gas pool as the contaminant front arrived at the bottom of the pool. As the pore interfaces at the lower boundary of the gas pool become contaminated with surfactant, weakened terminal pressures with their associated decreased capillary component of the hydraulic gradient, become unfavourable for imbibition, as few pore sites are available for withdrawing water. For gas migration to occur, imbibition must take place simultaneously to displace gas released. The combined effects of reduced gas pool height and limited imbibition result in the final termination of the gas pool to a critical height.

3.3.5 Effects of pre-existing gas release pathways and heterogeneities on gas migration and termination

Contaminating the quasi-saturated system with t-BuOH after subsequent mobilization experiments caused an entrapped gas pool to migrate through the capillary barrier, and the coarse porous medium at the top of the flow-cell, until the pool below the confining layer was completely drained (Figure 3.14). Migration of t-BuOH through the porous medium resulted in the contamination of the gas, resulting in a decrease in interfacial tensions of the pore scale gas-fluid interfaces. Mobilization was initiated after 88 minutes of t-BuOH transport in ExpT1, and 59 minutes in ExpT2, displayed as a decrease in the depth of the lower boundary of the gas pool (Figure 3.14.d). At these times, the approximate advective front computed had arrived at the top of the capillary barrier. Initiation of mobilization at low concentration of t-BuOH transported by hydrodynamic dispersion resulting in small decreases in interfacial tension was enough to trigger gas flow through the capillary barrier. A decrease in the height of the gas pool below the capillary barrier was observed over time as t-BuOH transported downwards through the porous medium, from an initial height of 7.8±0.4 cm in ExpT1 and 7.6±0.4 cm in ExpT2, to 0 cm in ExpT1 and ExpT2 (Figure 3.14.a-c).

Migration of gas was observed through a visible heterogeneity connected to the gas pool (Figure 3.15.a). The heterogeneity was comprised of a conglomerate of fingers in the center of the capillary barrier displayed as a lighter coloured region of lower water saturation. After the gas pool had mobilized from below the capillary barrier, gas release was still observed through the visible heterogeneity in the fine material, accompanied by corresponding bubbling at the surface of the flow-cell. As gas continued to migrate through the porous medium, the length of the heterogeneity in the fine material decreased as pores at the bottom of the fingers became saturated, visible as the pore paths began to darken in colour observed in both ExpT1 and ExpT2 (figure 3.15.b). The apparently connected continuous unsaturated region in the fine material extended to a measured depth of 4.3 ± 0.4 cm below the top of the capillary barrier after gas flow had terminated. Transport of gas through a saturated porous medium is controlled by the pathways and conduits that contain a connection of pores that impose the least resistance to migration of a non-wetting fluid. Disconnected gas tends to migrate through similar gas pathways, or fingers, when multiple release events take place in the same geologic depositional setting (Lao, X. 2011). As migration through the deposit continues, initially narrow finger paths widen as expulsion of gas through the same pathway further disrupts sediments. Further expansion of heterogeneities can result from the interception of unique fingers generated from different connected pore paths, merging to form a larger release path. Consecutive

gas migration through the same gas paths and adjacent fingers resulted in the formation of visible heterogeneity in the center of the capillary barrier that became connected to the gas pool when mobilization was initiated. The visible heterogeneity in the capillary barrier generated an extension of gas that extended to the top of the capillary barrier. This extension would exhibit much stronger buoyant forces, as the difference in hydrostatic pressure between the bottom of the gas pool and the top of the capillary barrier is much greater than that of a pool that only extends to the bottom of the capillary barrier. Stronger buoyant forces of an extended pool would enhance gas migration by allowing continuous exceedance of capillary forces of the capillary barrier as contaminated pores with reduced entry pressures at the top of the gas pool were easily exceeded. Assuming the gas pool extended to the top of the capillary barrier, at an initial pool height of 15 cm, the terminated pool height after contamination with t-BuOH would theoretically be 4.3 cm based on Equation 3.03. The experimental results from both t-BuOH experiments support the theoretical extended gas pool height in a scenario where the gas pool was extended as a result of a developed heterogeneity in the fine sand trapping layer.

3.3.6. Gas redistribution in the presence of an interfacial tension gradient

Contamination of an immobile gas pool trapped below a fine sand capillary barrier with EtOH at the top of the pool triggered the migration of gas to the surface of the flow-cell, causing a decrease in gas pool height with time from an initial measured height of 7.6 ± 0.4 cm to 2.8 ± 0.4 cm (Figure 3.16.a-h). EtOH migrated down through the porous medium as a sharp front with the flow of water, displayed as a region of darker coloured porous

medium migrating further through the flow-cell with time. After 100 minutes of infiltration, the visible dark coloured aqueous EtOH front migrated through the arms of the capillary barrier, contaminating only the edges of the gas pool (Figure 3.16.e). As aqueous EtOH transport was maintained, the front continued to migrate along the bottom of the gas pool, from the outer edges towards the center (Figure 3.16.f-g). After 110 minutes, gas began to redistribute, migrating towards the contaminated edges of the pool (Figure 3.16.f). Gas from the center of the gas pool flowed towards the edges of the pool during redistribution, accompanied by a corresponding imbibition event at pores along the center of the gas pool.

The increase in gas pool height at the left and right edges of the gas pool was accompanied by a corresponding decrease in gas pool height at the center of the gas pool over time (Figure 3.17). After 110 minutes, the center of the gas pool had decreased to 2.9 ± 0.4 cm, while the gas extended to 4.4 ± 0.4 cm in depth at the left and right edges of the pool. After 130 minutes, the center of the pool had decreased to 2.8 ± 0.4 cm, while the left and right edges of the gas pool extended to 4.4 ± 0.4 cm and 4.5 ± 0.4 cm respectively. The volume of gas remained constant during this time, in which any change in pool height was a result of gas redistribution. Arrival of the aqueous EtOH front at the outer edges of the gas pool prior to the center of the pool would result in a decrease in interfacial tension of pore interfaces along the outer edge of the gas pool while the center remained unchanged. This behaviour generated an interfacial tension gradient along the bottom of the gas pool, with a local maximum interfacial tension at the center of the boundary. Multiphase fluid flow established by an interfacial tension gradient along an

interface between two immiscible fluids is recognized in the literature as the "Marangoni effect" (Chang, Y., et al. 2019; Khosravi, M., et al. 2015). Reduced entry pressures of pores along the outer edges become favourable for gas invasion, and subsequent drainage. Uncontaminated pores in the center of the gas pool exhibiting high terminal pressures become favourable for imbibition simultaneously, resulting in a decrease in pool height at the center of the pool and increase in pool height at the edges.

Two-dimensional advective-dispersive transport of aqueous EtOH through the coarse sand porous medium is influenced by the presence of a structural heterogeneity of finer sand material in the flow-cell (Figure 3.18). The migration path of the aqueous EtOH front is displayed in Figure 3.18.a-c outlined in red, and visible as darker coloured porous medium. EtOH flowed past the finer sand capillary barrier through the coarser sand background material with time, when an applied hydraulic gradient an order of magnitude greater than other experiments, of 0.4, was applied to the flow-cell (Figure 3.18.a). Flow of aqueous EtOH through the coarser sand background material was faster than flow through the finer sand comprising the capillary barrier. After 25 minutes of infiltration, the aqueous EtOH front, outlined in red, would reach the outer edges of lower boundary of the gas pool before contaminating the top of the pool (Figure 3.18.b). At this time, the lower boundary of the gas pool extended along the edges of the arms of the capillary barrier, displayed as light coloured, unsaturated porous medium. After 40 minutes of infiltration, aqueous EtOH had contaminated the entire lower boundary of the gas pool and had migrated through the entire depth of the flow-cell, displayed as darker coloured background porous medium (Figure 3.18.d). The lower boundary of the gas

pool was observed as a region of lighter coloured, unsaturated pores, extending to a blurred lower boundary 10.1 ± 0.5 cm below the top of the capillary barrier. Marangoni effects along the boundary of the gas pool by contamination with aqueous EtOH were demonstrated in these results. Contaminated interfaces along the outer edges of the pool established an interfacial tension gradient and triggered the redistribution of gas towards pores with reduced entry pressures along the edges of the lower boundary. Imbibition of uncontaminated pores along the center of the gas pool occurred simultaneously, until the aqueous EtOH front contaminated the entire lower boundary of the gas. Reduced entry pressures along the bottom of the gas pool allowed for drainage along most of the pores in the lower boundary, causing reduced saturation with depth. As the entrapped air was closed off to interaction with the atmosphere, extension of the pool was a result of capillary pressure changes along the bottom of the pool, likely accompanied by expansion due to mass transfer of volatiles to the gas phase (Mumford et al., 2010).

As the aqueous EtOH front reached the upper boundary of the gas pool after 41 minutes of infiltration, mobilization of gas was initiated (Figure 3.18.e). As the aqueous EtOH front continued to migrate through the porous medium, gas pool height decreased with time as gas flowed through the porous medium (Figure 3.18.f-h). After the gas pool extended from the initial height of 7.9 ± 0.4 cm to 10.1 ± 0.5 cm, over 40 minutes, the gas pool was observed to decrease non-linearly with time from to the measured height of 3.9 ± 0.2 cm after 96 minutes (Figure 3.19). The decrease in pool height with time in ExpE2 exhibited a similar trend to ExpE1. Despite reduced terminal pressures of the coarse material at the contaminated lower boundary of the gas pool, increased buoyant

forces of the extended gas pool would easily overcome weakened capillary forces, exceeding reduced entry pressure in the capillary barrier upon arrival of the aqueous EtOH front at the top of the gas after 42 minutes. As gas pool height decreased with time, reduced buoyant forces of a smaller gas pool and limited imbibition due to weakened capillary pressures at the lower boundary would inhibit the migration of gas through the capillary barrier. The measured final pool height did not support the theoretical final pool height of the initial gas pool contaminated with aqueous EtOH based on Equation 3.03 (Table 3.9). However, assuming the initial gas pool was equal to that of the extended pool of 10.1 ± 0.5 cm, the theoretical terminal pool height after contamination with EtOH was computed to be 3.1 cm. This result was in closer agreement to the experimental terminal pool height of 3.9 ± 0.2 cm, further supporting the relationship between the critical contaminated gas pool height with induced reductions in interfacial tension.

3.3.7. The effect of infiltration of biofuel additive LNAPL contamination on gas pool behaviour

To demonstrate the effects of an LNAPL spill event on the mobilization of trapped gas in a quasi-saturated groundwater system, free phase 1-BuOH was pooled across the top of the flow-cell, infiltrating the system as both a free-phase LNAPL source and associated dissolved aqueous 1-BuOH front (Figure 3.20). The first-order approximation of contaminant breakthrough curves calculated using the Ogata-Banks advection-dispersion transport model displays the concentration of dissolved aqueous 1-BuOH at the upper boundary of the gas pool with time (Figure 3.20.d). Migration of the dissolved aqueous 1-BuOH front through the porous medium with time causes an increase in the concentration of 1-BuOH at the top of the gas pool, as infiltration through the flow-cell was maintained. As concentration increased at the top of the gas pool, interfacial tension decreased non-linearly based on Equation 3.11 (Figure 3.20.d). Mobilization was initiated as the dissolved aqueous 1-BuOH front arrived at the upper boundary of the gas pool after 28 minutes in ExpB1, 165 minutes in ExpB2, and 98 minutes in ExpB3 displayed as an initial decrease in gas pool height from the initial measured heights of 8.5 ± 0.4 cm, 8.4 ± 0.4 cm, and 7.7 ± 0.4 cm respectively (Figure 3.21). The contaminant front had just arrived at the upper boundary at times corresponding to initiation of gas flow, as hydrodynamic dispersion brought the arrival of low aqueous 1-BuOH concentrations (Figure 3.20.d). Small decreases in interfacial tension of pore interfaces at the upper boundary of the gas pool at low concentrations was enough to trigger gas migration. Minimal reduction in entry pressure required to initiate gas transport suggests the gas pool was near its threshold for mobilization, in which the largest available connected pore did not require considerable decrease in capillary pressure to trigger gas flow. However, based on the first approximation of contaminant transport using the Ogata-Banks model and Equation 3.11, a slightly larger reduction in interfacial tension was required to initiate gas flow in ExpB3 after 98 minutes of transport. The smaller initial gas pool measured beneath the capillary barrier would exhibit lower buoyant forces in comparison to ExpB1 and ExpB2. As a result, for mobilization to occur, further reductions in capillary forces would be required for buoyant forces to induce mobilization in ExpB3. In other words, greater reductions in interfacial tension at higher aqueous 1BuOH concentrations were required to reduce entry pressures of available pores to trigger gas flow.

Mobilization of gas was observed as bubbling at the surface of the flow-cell through connected fingers, with a corresponding decrease in gas pool height with time (Figure 3.21). Gas release occurred as discrete episodic events displayed as brief termination events during mobilization. Temporary termination was observed after 42 and 46 minutes in ExpB1, as a brief period of constant pool height (Figure 3.21). Temporary termination events were observed, more numerously, in ExpB2 and ExpB3 as brief plateaus in gas pool height decrease with time. Mobilization of gas through the capillary barrier, extending through the coarser background sand was frequently followed by fragmentation of connected gas fingers due to snap-off. For gas migration to be sustained, re-mobilization would have to be initiated again. Advancement of the 1-BuOH front through the flow-cell would open more available gas pathways for gas invasion at the upper boundary of the gas, and initiate gas flow once again. Slower arrival of the contaminant front in ExpB2 and ExpB3 gradually brought the arrival of higher aqueous 1-BuOH concentrations to the upper boundary of the gas pool, and a slow decrease in interfacial tension at the upper boundary of the gas pool (Figure 3.20.d). Remobilization following temporary termination of gas migration upon fragmentation and snap-off of connected fingers would not be triggered until reductions interfacial tensions further reduced entry pressures for gas invasion. Remobilization would only be initiated as higher aqueous 1-BuOH concentrations arrived at the upper boundary of the gas pool.

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Gas migration was terminated as the 1-BuOH front contaminated the entire gas pool at reduced measured pool height of 2.7 ± 0.2 cm in ExpB1, 1.5 ± 0.2 cm in ExpB2, and 1.2 ± 0.2 cm in ExpB3 (Figure 3.20.c). As discussed previously, termination of gas flow through the capillary barrier is a direct result of reduced buoyant forces of a smaller gas pool and limited imbibition at the bottom of the pool. As the gas pool height decreases with time, buoyant forces acting to mobilize the gas through the porous medium are reduced. For mobilization to be sustained, further reductions in interfacial tension are required to reduce opposing capillary forces and overcome resistance to flow. At high concentrations of aqueous 1-BuOH, further reductions in interfacial tension are smaller, and cannot sustain flow through the capillary barrier (Figure 3.1). In addition, contamination at the lower boundary of the gas pool results in a decrease in terminal pressures proportional to the reduction in interfacial tension of pore interfaces at the bottom of the pool. Reduced terminal pressures limit pore sites available for imbibition required for displacement of gas during migration.

In ExpB1, the contamination pool height ratio, $H_{F:I}$, of 0.32 ± 0.03 was proportional to the interfacial tension ratio 0.33, supporting the direct relationship of gas pool height with reductions in interfacial tension (Table 3.10). In contrast, ExpB2 and ExpB3 exhibited smaller final gas pool heights than expected based on the theoretical pool height (Equation 3.03). Smaller gas pools likely result from limited trapping efficiency of a modified capillary barrier. The effects of multiple expulsion events on the same sediment deposition could result in the disturbance of sediments within the capillary barrier resulting from preceding experiments conducted on the same packing arrangement. Continuous expulsion of gases through the same pathways observed through the center of the capillary barrier may have modified trapping efficiency of the fine sand. These effects may be validated by the reduced gas pool heights generated in ExpB2 and ExpB3, in which the generated gas pool height decreased with each experiment. Pore-scale variations resulting from disturbance of sediments after migration events could result in variabilities in the local pore saturation and structure, contributing to smaller terminal pool heights measured. Even small-scale variabilities in the capillary barrier and coarse material can impact migration, snap-off and termination of disconnected gas pools.

3.4. Conclusion

Flow-cell experiments were designed and conducted to investigate the effects of contamination by biofuel additives on the behaviour and migration of trapped gases below the water table. These laboratory experiments demonstrated the direct effects of concentration-dependent interfacial tension on the initiation, migration and termination of a trapped gas pool in a heterogeneous quasi-saturated porous medium. Contamination of a gas pool trapped below a capillary barrier with different dissolved biofuel additives; isobutanol, ethanol, and tertiary butanol, induced the mobilization of gas through the porous medium to the surface of the flow-cell. In these experiments, the mechanisms of gas flow were identified as a direct consequence of interfacial tension reductions at gas-fluid interfaces at pores along the boundaries of the gas pool. The arrival of dissolved aqueous surfactant at the upper boundary of the gas pool caused a reduction in entry pressures

proportional to the reduction in interfacial tension induced, opening favourable pore paths for gas escape. Continuous infiltration of each biofuel additive with time brought the arrival of higher concentrations at the upper boundary of the gas pool, causing a reduction in pool height with time as imbibition occurred at the lower boundary of the gas pool simultaneous to gas release. Gas escape paths, or gas fingers, became visibly more numerous as a more pore paths were opened as a direct consequence of higher concentrations, causing further reductions in entry pressures at the top of the gas pool. Gas flow terminated at a critical gas pool height that can be defined by the contaminated capillary pressures at the boundaries of the gas pool.

In each experiment, the reduction in critical gas pool height was proportional to the reduction in interfacial tension induced by each biofuel additive, expressed by the contaminated pool height ratio of the final gas pool height measured divided by the initial pool height measured. Contamination with iso-butanol/ ethanol caused a reduction in interfacial tension of 0.31. The contaminated pool height ratio of gas pools contaminated with these surfactants was 0.34 ± 0.04 (ExpI2) and 0.37 ± 0.07 (ExpE1), exhibiting a proportional relationship to the reduction in interfacial tension induced at contaminated interfaces. The mechanism of the termination of gas flow was determined to be a summative process, resulting from the combined effects of reduced buoyant forces of a reduced pool height and limited available imbibition sites of contaminated interfaces along the lower boundary of the gas pool. Reduced buoyant forces of a smaller gas pool limit the ability to overcome weakened capillary forces of contaminated interfaces at the top of the gas pool. At a critical final pool height, the reduced entry pressures of contaminated pores at the upper boundary of the gas pool cannot be overcome, terminating gas flow through the porous medium. In addition, arrival of the aqueous surfactant front at the lower boundary of the gas pool limits sites favourable for imbibition required to displace gas escaping from the pool.

The behaviour of immobilized gases in a porous medium were observed to be affected by pore-scale heterogeneities and variabilities. A visible heterogeneity developed in the finer material capillary barrier resulted in an apparent extension of the immobile gas pool to an approximate height of 15 cm. When contaminated with tertiary butanol, increased buoyant forces of an extended pool resulted in the complete mobilization of gas below the capillary barrier. Instead, the gas pool reduced to a pool height proportional to the decrease in interfacial tension induced by tertiary butanol of 0.29, to 4.3 cm. Similar findings were observed when an extension of the gas pool resulted when ethanol contaminated the lower boundary of the gas pool prior to the upper boundary. When the outer edges of the lower boundary of the trapped gas pool was contaminated with ethanol before the center of the pool, interfacial tensions were reduced only at interfaces in pores along the edges of the gas. This established a concentration gradient, that would cause gas redistribution to the edges of the gas pool. Contamination along the bottom of the gas pool would establish an extended pool height to 10.1 ± 0.5 cm below the top of the capillary barrier. When mobilized, gas pool height decreased proportional to the reduction in interfacial tension of the extended gas pool, to a final measured pool height of 3.9 ± 0.2 cm. Despite heterogeneities or redistribution of gases

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generating an extended pool, the results of these experiments support the direct relationship of critical pool height and interfacial tension reductions.

When the quasi-saturated porous medium was contaminated with free-phase LNAPL, 1-butanol, the mechanisms and behaviour of gas flow through the porous medium was similar to contamination with dissolved aqueous surfactants. Contamination of dissolved aqueous 1-butanol at the upper boundary of the gas pool triggered mobilization by reducing entry pressures of pores along the bottom of the capillary barrier. Gas migrated through the contaminated system until terminating at a pool height proportional to the reduction in interfacial tension induced by 1-butanol. These experiments suggest that spill events with free-phase biofuel additives or biodiesel will not considerably influence the behaviours of gas flow, in which mobilization of gases below the subsurface will still result from contamination by dissolved chemical constituents.

As the use of biofuels and biofuel additives become more apparent in the oil and gas industry, an advanced understanding of the behaviours and interactions of the modern chemical constituents with groundwater components becomes increasingly important. The implications of contamination of quasi-saturated groundwater systems with chemical surfactants has the capacity to alter unique hydraulic properties that define an aquifer system by initiating mobilization of trapped gases below the water table. This can lead to a misrepresentation of the hydraulic properties characterizing a groundwater system, including; hydraulic conductivity, permeability, and diffusivity of solutes. Further work may apply these theories to other trapped residual non-wetting fluids below the water table, including both dense non-aqueous fluids, and LNAPLs, to further understand similar displacement mechanisms resulting from contamination with chemical surfactants and biofuel additives. Trapped gases can be generated in multiple depositional settings and are expected to exhibit behaviours unique to the porous medium in which they are immobilized. Further expanding upon this work by investigating the influence and behaviours of gases trapped in different geologic depositions with different capillary barrier geometries will provide further conceptualization of what may observed in a natural quasi-saturated groundwater system. Additionally, since the dynamic behaviour and implications of contact angle effects on capillary pressure remains a growing area of research, future work may also expand upon contact angle effects on gas migration to better isolate the processes driving gas transport in quasi-saturated groundwater systems. As biofuel additives continue to be an increasingly attractive alternative to fully petroleum-based fuels, the effects and consequences of the interactions that take place between the constituents and groundwater systems will remain a critical area of research.

Chemical	Water	Ethanol	Tertiary	Iso-Butanol	1-Butanol
properties at 25°C			Butanol		
Concentration	-	100	50	8	8
applied (% w/w)					
Surface tension	72.6 ¹	22.8^{1}	21.6 ²	22.45	23.77
(m·Nm)					
Density (g·cm ³)	1.01	0.79^{1}	0.83 ³	0.815	0.817
Viscosity (m·Pas)	1.01	1.201	4.69 ³	4.316	2.807
Vapour pressure	2.33 ¹	5.8 ¹	6.314	1.391	0.918
(kPa)					
Octane number	-	108	105	113	96

3.5. Figure	es and tables	
Table 3.1.	Chemical properties of biofuel additives at 25°	УC

1. Kadlec, P., et al. 2010; 2. Gliński, J., et al. 1995; 3. Kipkemboi, P. K., et al. 1995; 4. Kruus, P., & Hayes, C. A. 1985; 5. Bermúdez-Salguero, C., et al. 2011; 6. Jin, C., et al. 2011; 7. Bikerman, J. J. 1970; 8. Butler, J. A. V., et al. 1935; 9. Liu, H., et al. 2016



Figure 3.1. *Interfacial tension dependent concentration curves for applied biofuel additives.* The purple, solid line displays the 1-BuOH curve, blue, large dashed line displays the EtOH curve, the green, small dashed line displays the iso-BuOH curve, and the orange, dotted line displays the t-BuOH curve.



Figure 3.2. *Flow-cell apparatus and sand packing dimensions*. Sand packing arrangements for aqueous and LNAPL contamination, where dark grey material represents Opta 56.3.10 fine sand, light grey is GS-20 coarse sand, and white dotted is B.P. T18.7 coarse sand. Sand packing number one is characterized by an 8.0 cm thick entrapment layer, for use in aqueous contamination (a). Sand packing number two is characterized by a 4.0 cm thick entrapment layer, for use in LNAPL contamination (b).



Figure 3.3. *Flow-cell packing method equipment and design*. Material labelled from 1 to 9 in the order of pour. Custom wooden barrier affixed to the top of the flow cell to ease pour and minimize spill over of sand. Four wooden dowels used to stabilize and support fine entrapment layer arms, with fitted textile pieces to block intrusion of coarse sand.



Figure 3.4. *Schematic diagram of hanging water column apparatus.* 100 mL burette filled with water to the surface of the sand column in a Buchner funnel, hydraulically connected using tygon tubing. A meter stick was aligned at the 0 cm mark with the surface of the sand column.



Figure 3.5. Schematic diagram of constant head infiltration flow-cell experimental setup. Flow-cell contamination experiments were conducted by infiltrating surfactant through the surface of sand pack using a constant head method. A piezometer aligned with a meter stick was used to record pressure data, connected to the output tygon tubing. The output beaker was placed atop a scale to measure discharge.



Figure 3.6.a. *Saturated flush of contaminated sand through the top of the flow cell*. A peristaltic pumped connected to the ponded surface removed contaminant at a constant rate, establishing an upwards flow of fluid. Clean water was introduced to the bottom of the cell, displacing contaminated pores upon flow.



Figure 3.6.b. Unsaturated flush to induce isolated contaminant displacement in fine entrapment layer. Photos, i. to iii., display the response to water infiltration in the unsaturated media when 60 mL was added to point source. Photos, iv. to vi., display the response when water was targeted to flush the arms of the fine entrapment layer.

Table 5.2. Flow cell packing arrangement parameters.							
Volume of Flow-cell (cm ³)	Mass of sand (g)	Bulk density of Flow-cell (cm ³)	Porosity of Flow-cell (%)				
Packing arrangement No. 1							
2905.7	4970.7	1.7	35.8				
Packing arrangement No. 2							
2905.7	5068.9	1.7	35.8				

 Table 3.2. Flow cell packing arrangement parameters.

 Table 3.3. Hanging water column sand core parameters.

	Coarse sand	Fine sand		
Soil core parameters	Opta Minerals sand	Bell & McKenzie sand GS-20		
	56.3.10			
Grain material	Silica sand	Silica sand		
Height (cm)	3.0	3.3		
Volume (cm ³)	170.2	187.1		
Bulk density (g·cm ⁻³)	1.7	1.6		
Porosity (%)	37.0	39.5		

Table 3.4. *Initial conditions of all experiments conducted*. Includes initial measured gas pool heights, biofuel alcohol dilutions, and the applied hydraulic gradient initially in all experiments. Concentrations of each alcohol were established based on the solubility of each compound in order to establish aqueous solution for contamination. Contaminants were prepared in 2-L volumes and prepared for each experiment.

Surfactant	Experiment	Initial gas pool height (cm)	Mass of alcohol (g)	Mass of water (g)	Concentration w/w (%)	dh dl (gradient)
EtOH	ExpE1	7.6±0.4	-	-	100	0.05
	ExpE2	7.9±0.4	-	-	100	0.4
Iso-BuOH -	ExpI1	7.4±0.4	136.20	1836.9	6.9	0.04
	ExpI2	7.6±0.4	161.5	2023.5	7.9	0.02
t-BuOH -	ExpT1	7.8±0.4	990.3	1007.7	49.6	0.04
	ExpT2	7.6±0.4	970.8	1036.0	48.4	0.09
1-BuOH	ExpB1	8.5±0.4	-	-	7.4	0.09
	ExpB2	8.4±0.4	-	-	7.4	0.05
	ExpB3	7.7±0.4	-	-	7.4	0.07



Figure 3.7. Measured and modelled capillary pressure-saturation (P_C -S) curves for GS-20 sands in hanging water column experiments. The red-dotted line displays the measured wetting curve from the hanging water column, and the red-solid line displays the Brooks-Corey fit wetting curve. The blue-dotted line displays the measured draining curve from the hanging water column, and the blue-solid line displays the Brooks-Corey fit draining curve.



Figure 3.8. Measured and modelled capillary pressure-saturation (P_C -S) curves for Opta-56 sands in hanging water column experiments. The red-dotted line displays the measured wetting curve from the hanging water column, and the red-solid line displays the Brooks-Corey fit wetting curve. The blue-dotted line displays the measured draining curve from the hanging water column, and the blue-solid line displays the Brooks-Corey fit draining curve.

Retention curve parameters		Coarse sand		Fine sand	
		Drainage	Wetting	Drainage	Wetting
Rewetted saturation (-)	$\theta_{\rm S}$	0.35	0.37	0.32	0.33
Alpha	α	0.10	0.21	0.04	0.08
n		4.69	4.69	1.20	1.20
Entry pressure (cm)	Pe	10.36	-	20.92	-
Terminal pressure (cm)	Pt	-	4.73	-	12.9
Pt:Pe Ratio		0.46		0.58	
R ²		0.99	0.95	0.97	0.97

 Table 3.5. Retention curve parameters from RETC curve fit at 95% confidence.


Figure 3.9. *Mobilization of gas and decrease in pool height upon contamination with aqueous surfactants iso-BuOH and EtOH*. Decrease in gas pool height with increased concentration overtime in (a) initial pool height, (b) pool height after mobilization of 50% of trapped gas, (c) terminal pool height in response to surfactant contamination. Advective-based transport of dissolved surfactant constituents, where red displays the computed advective front and green displays the measured depth of the lower boundary in iso-BuOH experiments of the gas pool over time, and blue in the EtOH experiment (d).



Figure 3.10. Unique finger pathway generated in experiment 2 when contaminated with iso-BuOH. A distinct gas pathway was visible in the coarse sand as a region of contrasting refractive index, lined in blue. Bubbling at the surface of the sand pack was observed releasing to the left of the gas pool, circled in red.



Figure 3.11. *Visible gas fingers generated from EtOH infiltration*. As EtOH infiltrated further through the flow-cell with time, new gas release paths are generated based on favourable connected pore paths. Finger(s) generated after (a) 41 minutes, (b) 41.25 minutes, (c) 41.45 minutes, (d) 44.18 minutes, (e) 51.13 minutes, (f) 63.15 minutes.

Table 3.6. Theoretical final gas pool heights assuming initial measured gas pool height
and experimental measured final gas pool height after complete contamination with
aqueous surfactants.

Experiment	$\frac{\sigma_s}{\sigma_w}$	Contaminated pool height ratio (H _{F:I})	Theoretical pool height of contaminated system (cm)	Final measured pool height (cm)
ExpI1	0.31	0.46 ± 0.05	2.4	3.4 <u>±</u> 0.2
ExpI2	0.31	0.34 ± 0.04	2.4	2.6±0.2
ExpE1	0.31	0.37 ± 0.07	2.4	2.8±0.4

Table 3.7. Theoretical final gas pool heights assuming initial wetting conditions and experimental measured final gas pool height after complete contamination with aqueous surfactants.

	Final gas pool height (cm)							
	No contamination (theoretical)	Top contamination (theoretical)	Bottom contamination (theoretical)	Complete contamination (theoretical)	Experimental measured			
ExpI1	8.3	-0.9	15.0	3.3	3.4 <u>±</u> 0.2			
ExpI2	8.3	-0.9	15.0	3.3	2.6 <u>±</u> 0.2			
ExpE1	8.3	-0.9	15.0	3.3	2.8 <u>±</u> 0.4			

 Table 3.8. Critical capillary, bond and trapping numbers computed for prior to and during mobilization of gas for experiments contaminated with aqueous surfactant.

		Prior to gas migration							
	dh dl (gradient)	Capillary Number	Bond Number	Trapping Number					
ExpI1	0.04	2.5×10^{-11}	6.1×10^{-7}	6.1×10^{-7}					
ExpI1	0.02	4.7×10^{-11}	2.9×10^{-6}	2.9×10^{-6}					
ExpE1	0.05	1.3×10^{-8}	4.2×10^{-4}	4.2×10^{-4}					
ExpT1	0.04	1.5×10^{-12}	3.4×10^{-8}	3.4×10^{-8}					
ExpT2	0.09	$5.6 imes 10^{-11}$	6.2×10^{-7}	6.2×10^{-7}					
		During g	as migration						
	dh dl (gradient)	During g Capillary Number	as migration Bond Number	Trapping Number					
ExpI1	<u>dh</u> <u>dl</u> (gradient) 0.01	During g Capillary Number 3.4×10^{-10}	as migration Bond Number 2.4×10^{-5}	Trapping Number 2.4×10^{-5}					
ExpI1 ExpI1	dh dl (gradient) 0.01 0.03	During g Capillary Number 3.4×10^{-10} 4.2×10^{-10}	as migration Bond Number 2.4×10^{-5} 1.2×10^{-5}	Trapping Number 2.4×10^{-5} 1.2×10^{-5}					
ExpI1 ExpI1 ExpE1	dh dl (gradient) 0.01 0.03 0.07	During g Capillary Number 3.4×10^{-10} 4.2×10^{-10} 3.4×10^{-7}	as migration Bond Number 2.4×10^{-5} 1.2×10^{-5} 3.8×10^{-3}	2.4 × 10 ⁻⁵ 1.2 × 10 ⁻⁵ 3.8 × 10 ⁻³					
ExpI1 ExpI1 ExpE1 ExpT1	dh dl (gradient) 0.01 0.03 0.07 0.02	During g Capillary Number 3.4×10^{-10} 4.2×10^{-10} 3.4×10^{-7} 1.0×10^{-10}	as migration Bond Number 2.4×10^{-5} 1.2×10^{-5} 3.8×10^{-3} 4.1×10^{-6}	2.4 × 10 ⁻⁵ 1.2×10^{-5} 3.8×10^{-3} 4.1×10^{-6}					



Figure 3.12. *Measured decrease in gas pool height with time upon contamination with aqueous surfactants.* Decrease in gas pool height was observed upon the arrival of contamination. Contamination with t-BuOH in ExpT1 displayed as dark orange-solid line with dots, and ExpT2 as light orange-dashed line with triangles. Contamination with iso-BuOH in ExpI1 displayed as dark green, solid line with dots, and ExpI2 as light green dashed line with triangles. Contamination with etoH in ExpE1 displayed as blue solid line with dots.



Figure 3.13. *Measured discharge rates through the flow-cell throughout gas mobilization upon contamination with aqueous surfactants.* Contamination with t-BuOH in ExpT1 displayed as dark orange, solid line with dots, and ExpT2 as light orange-dashed line with triangles. Contamination with iso-BuOH in ExpI2 as light green dashed line with triangles. Contamination with EtOH in ExpE1 displayed as blue solid line with dots.



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Figure 3.14. *Mobilization of gas and decrease in pool height upon contamination with aqueous surfactant t-BuOH*. Decrease in gas pool height with increased concentration overtime in (a) initial pool height, (b) pool height after mobilization of 50% of trapped gas, (c) terminal pool height in response to surfactant contamination. Advective-based transport of dissolved surfactant constituents, where red displays the computed advective front and orange displays the measured depth of the lower boundary of the gas pool over time (d).



Figure 3.15. Gas transport through visible extended gas pathway in the center of the capillary barrier upon contamination with t-BuOH (from ExpT1). (a) Visible gas release through the center of the extended gas pool with bubbling observed at the surface of the sand pack from connected pathway, circled in red; (b) Unsaturated region in fine

	Time (minutes)	Pool height (cm)	Mobilization		Time (minutes)	Pool height (cm)	Redistribution after to mobilization
a.	30	7.6 ±0.4		e.	100	3.3 ±0.2	
b.	55	4.5 ±0.2		f.	110	2.9 ±0.4	
c.	70	3.5 ±0.2		g.	120	2.8 ±0.4	
d.	95	3.5 ±0.2		h.	130	2.8 ±0.4	

sand corresponding to theoretical terminal gas pool height upon contamination with t-BuOH.

Figure 3.16. Decrease in gas pool height and redistribution of gas at the lower boundary of the pool upon slow contaminant infiltration of EtOH (Experiment 1).



Figure 3.17. *Redistribution of gas pool in EtOH experiment 1 measured as change in height along the bottom of the pool.* Decrease in pool height at the center of the gas pool, solid black line with circles, observed as proportional increases in pool height at the left and right edges of the gas, grey dashed with triangles and grey dotted line respectively.

	Time	Pool height	Dedictribution prior to mehilization		Time	Pool height	
	(minutes)	(cm)	Redistribution prior to mobilization		(minutes)	(cm)	Mobilization
a.	15	7.9 ±0.4		e.	50	8.6 ±0.5	
b.	25	8.2 ±0.5		f.	70	7.8 ±0.5	
c.	30	8.3 ±0.5		g.	90	4.3 ±0.2	
d.	40	10.1 ±0.5		h.	100	3.9 ±0.2	

Figure 3.18. *Decrease in gas pool height and redistribution of gas at the lower boundary of the pool upon fast contaminant infiltration of EtOH (ExpE2).* The gradual extension of the gas pool was outlined in red to display the visible redistribution in gas saturation upon contamination of EtOH in ExpE2



Figure 3.19. *Measured contaminated pool height ratio with time upon contamination with EtOH in different hydraulic regimes.* Decrease in gas pool height was observed upon the arrival of contamination with EtOH in ExpE1, solid dark blue line and dots. Initial increase in gas pool height observed upon continuation of EtOH at the bottom of the gas pool prior to the top in ExpE2, light blue-dashed line and triangles. Consecutive decrease in pool height observed upon arrival of EtOH at the upper boundary of the gas pool.

	$\frac{\sigma_s}{\sigma_w}$	Contaminated pool height ratio (H _{F:I})	Theoretical pool height of contaminated system (cm)	Final measured pool height (cm)
ExpE1	0.31	0.37±0.05	2.4	2.8±0.4
ExpE2	0.31	0.49±0.05	2.4	3.9 <u>±</u> 0.2
	$rac{\sigma_s}{\sigma_w}$	Contaminated pool height ratio based on expanded pool (H _{F:1})	Theoretical pool height of contaminated system <i>based</i> <i>on expanded pool</i> (cm)	Final measured pool height (cm)
Exp E2	0.31	0.39±0.04	3.1	3.9±0.2

Table 3.9. Theoretical final gas pool heights assuming initial measured gas pool heightand experimental measured final gas pool height after complete contamination withEtOH.



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Figure 3.20. *Mobilization of gas and decrease in pool height upon contamination with 1-BuOH*. Decrease in gas pool height with increased concentration overtime in (a) initial pool height, (b) pool height after mobilization of 50% of trapped gas, (c) terminal pool height in response to surfactant contamination. Contaminant breakthrough curve and corresponding interfacial tension with time through the flow-cell domain (d).



Figure 3.21. *Decrease in gas pool height with time upon contamination with 1-BuOH.* Contamination with 1-BuOH in ExpB1 displayed as purple-solid line and dots, ExpB2 as purple-dashed line and triangles, and ExpB3 as purpled-dotted line and blocks.

Table 3.10. Theoretical final gas pool heights assuming initial measured gas pool
height and experimental measured final gas pool height after complete contamination
with 1-BuOH.

	$\frac{\sigma_s}{\sigma_w}$	Contaminated pool height ratio (H _{F:1})	Complete contamination (theoretical)	Final measured pool height (cm)
ExpB1	0.33	0.32 ± 0.03	2.8	2.7 <u>±</u> 0.2
ExpB2	0.33	0.18±0.03	2.8	1.5±0.2
ExpB3	0.33	0.16±0.03	2.6	1.2±0.2

3.6. References

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Chapter 4: Modelling gas mobilization and migration Abstract

Extensive analyses conducted have identified 1-butanol as one of the most favourable fuel additives for combustion engines, having the capacity to improve combustion efficiency, reduce emissions from exhaust, and prevent phase separation in fuels. As 1-butanol continues to be administered as an additive in gasoline and diesel fuels, the risk of contamination by 1-butanol in groundwater systems increases. It is critical to understand the interactions that take place between 1-butanol and components of potable groundwater systems. A macroscopic invasion percolation model was combined with an advection-dispersion model to simulate the migration of an initially immobile gas pool, including the initiation and termination of gas flow. The model accounted for the concentration-dependent reduction in air-water interfacial tension due to the transport of aqueous 1-butanol, decreasing the capillary entry pressures assigned to the domain in proportion to interfacial tension. Simulations showed the initiation of gas migration upon the arrival of the 1-butanol contaminant front at the upper boundary of the gas pool. Gas release occurred through multiple connected pores in fingers generated based on the most favourable entry pressure pathways. The reduction in gas pool height was proportional to the reduction in interfacial tension induced by the surfactant properties of 1-butanol. Simulations showed an initial pool to final pool height ratio of 0.39 ± 0.08 , which agreed well with the measured ratio from experiments of 0.32 ± 0.02 . The model was able to simulate key components observed in flow-cell experiments, demonstrating the flow behaviour and termination of a disconnected gas pool contaminated with 1-butanol.

4.1. Introduction

As environmental regulations on global greenhouse gases (GHG) emissions continue to become more stringent, the demand for alternative and improved fuel sources continues to rise. Renewable fuels and low emission technologies continue to be an extensive and critical area of research as vehicular emissions remain the primary source of GHGs (Jenn et al., 2019). Biofuels and biofuel additives are being introduced to gasoline and diesel fuels in the forms of biofuel-gasoline, biodiesel blends, and biofuel oxygenate additives to improve automotive efficiency, and limit emission of GHGs and human carcinogens (Liu et al. 2016; Rakopoulos et al. 2010; Westphal et al. 2010; Yang et al. 2016; Yilmaz et al. 2014). Biofuel additives often consist of alcohol oxygenates, and are introduced to gasoline in a range of concentrations to optimize engine combustion efficiency and octane numbers, while reducing smoke opacity (Yang et al. 2016), emissions of polycyclic aromatic hydrocarbons (PAH), carbon monoxide (CO), benzene, and particulate matter (PM) (Westphal et al. 2010). Biofuel additives are generated from a range of renewable sources including vegetable waste, wood, corns, and cooking oils (Elfasakhany, 2014). The most common biofuel oxygenate additive being administered to gasoline and diesel fuels is ethanol, defined by its high octane number and ability to limit vehicular emissions (Liu et al. 2016). However, recent work has identified numerous disadvantages to ethanol in comparison to higher alcohols characterized by larger carbon chains and higher molecular weight (Christensen et al., 2011; Lui et al. 2016; Yang et al. 2016). Higher alcohols are being considered as an alternative additive to methanol and ethanol due to their higher energy density, lower vapour pressure, and reduced solubility in water

(Christensen, et al. 2011). These attributes allow for improved fuel efficiency, reduced evaporative emissions, and enhanced seasonality of fuels. Many studies have observed optimal performance upon use of 1-butanol (1-BuOH) in both gasoline and diesel fuels as an alternative to bioethanol (Christensen et al., 2011; Jin et al., 2011; Rakopoulos et al., 2010; Yilmaz et al., 2014). Unlike lower alcohols, butanol has a greater miscibility with diesel, preventing phase separation and reduction of combustion efficiency. These defining properties in fuels result from the larger hydrocarbon chain and the presence of an attached hydroxyl moiety, providing unique chemical behaviours favourable for improved efficiency in combustion engines. As 1-BuOH begins to be added to fuels, it will begin to appear in groundwater contaminated from spills and leaks from underground storage tanks, pipelines, and transportation accidents (Potter, 1996). The chemical properties of 1-BuOH characterize it as a surfactant, influencing fate and transport in groundwater systems.

Chemical surfactants are compounds that have a high affinity to adsorb to an interface between two immiscible fluids, and induce a reduction interfacial energies by modifying adhesion and cohesion forces along an interface (Rosen & Kunjappu, 2012). The amphipathic nature of surfactant molecules, with a hydrophobic tail and hydrophilic functional group, results in interactions with both non-polar and polar fluids, respectively. Sorption of surfactant molecules at an interface results in a decrease in interfacial energies, and a corresponding decrease in interfacial tension. The reduction in interfacial tension in the presence of a chemical surfactant is a concentration-dependent process, such that as the concentration of surfactant at the interface increases, a non-linear decrease in interfacial tension results (Eastoe, J., & Dalton, J. S. 2000, Phan, C.M., et al. 2016). The extent of interfacial tension reduction differs among surfactants. 1-BuOH causes a decrease in interfacial tension from that of clean water from 73 mN·m⁻¹ to 23.7 mN·m⁻¹ at its aqueous solubility (Figure 4.1). The tendency of surfactants to diffuse towards an immiscible fluid interface can have implications on unsaturated groundwater systems, including those containing trapped non-wetting fluids. In addition to accidental releases of surfactants, surfactants have also been administered to contaminated groundwater systems to enhance recovery of immobile non-aqueous phase liquids (NAPLs) by inducing a decrease in interfacial tension along the NAPL-water interface and re-mobilizing trapped fluids (Pennel et al., 1993).

Trapped gases can be generated in groundwater systems both naturally and anthropogenically from byproducts of biological activity and decomposition of organics, artificial groundwater recharge, soil swelling, water table fluctuations, and gas injection remediation methods (Dunn & Silliman, 2003; Faybishenko, 1995; Marinas et al., 2013; McLeod et al., 2015). Groundwater systems containing immobile gases have previously been referred to as quasi-saturated zones, characterized as shallow groundwater zones where entrapped gases are generated and sustained due to low hydrostatic pressures (Gonçalves et al., 2020). As such, they are unsaturated zones, but importantly, gasoccupied regions are not connected over large scales and are not connected to the atmosphere. The trapping of disconnected gases depends on the balance of capillary forces acting to retain the gas, and buoyant forces acting to induce migration (Roy & Smith, 2007). Studies have observed mobilization of previously trapped gases as a result of gas expansion as a consequence of mass transfer of volatiles to the gas phase, in which increased buoyancy drives gas flow (Mumford et al., 2010; Roy & Smith, 2007). Mobilization of trapped gases has been observed to alter the hydraulic properties characterizing a hydrogeologic system causing decreases in hydraulic conductivity, decreases in permeability, and increases in dispersivity of solutes (Faybishenko, 1995; Gonçalves et al., 2020; Klenk et al., 2002; Marinas et al., 2013). These changes can have effects on site characterization and monitoring in practical settings, leading to the misrepresentation of groundwater systems.

Gas migration and flow behaviours have been simulated using different modelling techniques to understand the fundamental mechanisms and interactions contributing to gas flow phenomena, including using models based on invasion percolation (IP) (Ewing & Gupta, 1993; Glass et al., 2001; Ioannidis et al., 1996; Kueper & McWhorter, 1992; Larson et al., 1981; Mumford et al., 2010; Wilkinson & Willemsen, 1983). IP models were one of the early models developed to simulate the transport of non-wetting fluids through saturated media at the pore scale (Ewing & Gupta, 1993; Ioannidis et al., 1996; Wilkinson & Willemsen, 1983). In these models, gas flow is simulated through a series of invasion steps (drainage or imbibition) within a pore network generated based on the pore size distribution and soil properties of a porous medium. Early IP models constructed pore networks as a series of connected sites (nodes) and bonds with characteristic radii assigned randomly (Wilkinson & Willemsen, 1983). The sites and bonds represent individual pores and pore throats allowing for analysis and interpretation of pore scale dynamics during multiphase fluid flow. Fluid advancement is simulated in a

series of steps determined by the size of the pores and throats. Non-wetting fluid invades connected sites with the largest radii that are saturated with water, while water displaces non-wetting fluid at the sites with the smallest radii. While the complexity of IP models provides great insight on pore-scale phenomena, it is limited to small-scale applications. To conduct multiphase flow simulations on larger-scale problems, macroscopic-IP (MIP) models have been developed, in which the porous network is divided into a series of subpore networks (Glass et al., 2001; Ioannidis et al., 1996; Kueper & McWhorter, 1992). Rather than assigning individual radii to pores and throats, MIP assigns material properties extracted from capillary-pressure saturation relationships to produce a volumeaveraged model (Glass et al., 2001; Kueper & McWhorter, 1992). The MIP algorithm uses the same mechanism for gas migration as IP models, in which the gas invades a connected block with the lowest entry pressure, while water displaces gas in connected blocks with the lowest terminal pressure (Glass et al., 2001; Mumford et al., 2010). MIP applied to NAPL contaminated systems has successfully modelled gas flow behaviours in the presence of volatile constituents (Krol et al., 2011; Molnar et al., 2019; Mumford et al., 2010) but there have been no studies that have incorporated concentration-dependent interfacial tension to account for surfactant transport.

Understanding the interactions that take place with emerging contaminants and groundwater components is crucial for developing remediation techniques and policies to protect groundwater resources. The effects of surfactant contamination on the stability and transport of disconnected gases in quasi-saturated groundwater zones may have several consequences on the hydraulic properties that characterize a flow system. For

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example, the mobilization of trapped gases may result from several processes including gas expansion or weakening of a gas-water interface by reductions in interfacial tension, allowing buoyant forces to overcome retaining capillary forces (Roy & Smith, 2007). It is hypothesized that as a 1-BuOH contaminant front approaches the upper boundary of an immobile gas, weakened air-fluid interfaces will facilitate the migration of gas through saturated pores. There have been no studies reported in the literature that have simulated the effects of reduced interfacial tension in the presence of a chemical surfactant on the behaviour and flow of disconnected gases below the water table using MIP modelling techniques. However, as the use of biofuel additives in gasoline and fuel products continues to become more prevalent, the interactions and mechanisms controlling trapped fluid transport in groundwater systems becomes important.

The objectives of this work were to: 1) modify the MIP model developed by Mumford et al. (2010) to incorporate concentration-dependent interfacial tension changes, 2) simulate the effects of interfacial tension reduction on the behaviour of an entrapped gas pool in response to contamination by 1-butanol during flow-cell experiments using the developed MIP-interfacial tension (MIP-IFT) model, and 3) perform a sensitivity analysis to determine the critical parameters in gas migration induced by decreases in interfacial tension.

4.2. Development of numerical model

4.2.1. Aqueous transport

The MIP-IFT model accounted for the transport of dissolved surfactant as well as the migration of a disconnected gas phase. Solute transport was simulated assuming onedimensional vertical transport using the advection-dispersion equation (Fetter et al., 1999):

$$D_L \frac{\partial^2 c}{\partial z^2} - \bar{v}_z \frac{\partial c}{\partial z} = \frac{\partial c}{\partial t}$$
(4.01)

where C (ML⁻³) is the concentration of the dissolved solute, \bar{v} (MT⁻¹) is the average linear pore water velocity, D_L (-) is the longitudinal dispersion coefficient, z (L) is the depth, and t (T) is time. Prior to contaminant transport, it was assumed that the porous medium was uncontaminated, such that the concentration of solute across the entire system was zero:

$$C(x,0) = 0, x \ge 0 \tag{4.02}$$

Throughout solute transport, it was assumed that a semi-infinite boundary existed across the porous medium, in which the contaminant existed as a continuous source zone at the surface of the system, inhibiting depletion during migration:

$$C(0,t) = C_0, \ t \ge 0 \tag{4.03}$$

$$\mathcal{C}(\infty, t) = 0, \ t \ge 0 \tag{4.04}$$

The Ogata-Banks analytical solution (Fetter et al. 1999) was used to solve equation 4.01:

$$C = 0.5C_0 \left[erfc \left(\frac{L - \bar{v}t}{2\sqrt{D_L t}} \right) - e^{\left(\frac{\bar{v}L}{D_L} \right)} erfc \left(\frac{L + \bar{v}t}{2\sqrt{D_L t}} \right) \right]$$
(4.05)

where C_0 (ML⁻³) is the concentration of dissolved solute at the top boundary and L (L) is the distance of transport for the average particle. The 1-BuOH pool was represented in the model as a boundary of 100% concentration maintained at a constant depth to represent the boundary established in experiments. The concentration was computed at each grid block in the model, advancing with depth through the porous network, while remaining constant laterally across the domain.

4.2.2. Concentration dependent interfacial tension

Migration of a chemical surfactant will induce a non-linear decrease in interfacial tension upon arrival at an immiscible fluid interface. To simulate the effects of concentrationdependent interfacial tension on transport of a trapped fluid in a quasi-saturated porous medium, interfacial tension was computed at each grid block over time. Following computation of concentration in a 1-BuOH contaminated system, interfacial tension was computed based on a concentration-dependent interfacial tension relationship for 1-BuOH (Smith & Gillham, 1999):

$$\sigma = \sigma_w \left(1 - b \left(\ln \left(\frac{c}{a} + 1 \right) \right) \right) \tag{4.06}$$

where σ_w (MT⁻²) is the uncontaminated air-water interfacial tension, and *a* (-) and *b* (-) are parametric constants specific to 1-BuOH. The concentration-dependent interfacial tension relationship differs between surfactants due to unique chemical properties and surfactant strengths. As interfacial tension depends directly on the mass transport of solute, the interfacial tension changed with depth and time, and did not vary laterally across the porous network.

4.2.3. Entry and terminal pressures

To represent a real porous medium in the MIP model, defining material properties were assigned to the pore network to best capture the behaviours of a physical system. The porous network was represented by a series of grid blocks that were either occupied by water or by gas and water, with a connectivity of four. Each grid block was randomly assigned a characteristic capillary pressure based on capillary pressure-saturation relationships measured for each material (Chapter 3, Elliott & Smith, 2020; Gerhard & Kueper, 2003). Inverse transform sampling was used to assign random capillary pressures to each grid block, where the cumulative distribution function was computed based on the Brooks-Corey capillary-pressure saturation model (Brooks & Corey., 1964):

$$\left(\frac{P_c}{P_d}\right)^{-\lambda} = \frac{(S_w - S_{wr})}{(1 - S_{wr})} \tag{4.07}$$

where $P_c(L)$ is capillary pressure expressed as an equivalent height of water, $P_d(L)$ is the displacement pressure of the material, $S_w(-)$ is the saturation of wetting fluid, $S_{wr}(-)$ is the residual saturation of wetting fluid, and $\lambda(-)$ is a parameter representing the pore-size distribution of the medium. As inverse transform sampling performs well for primarily uniform porous materials, the range of entry pressures assigned to the capillary barrier was constrained by assigning a λ value greater than that measured from experiments to the model. This ensured the macroscopic entry and terminal pressures were captured by grid blocks comprising the capillary barrier in the model domain. The inverse transform sampling method is limited to uniform materials and could not capture the behaviours of a wider pore size distribution exhibited by the material comprising the capillary barrier.

The assigned capillary pressures relate to pore scale dynamics, responding directly to variability in interfacial tension:

$$P_c = \frac{2\sigma \cos\theta}{R} \tag{4.08a}$$

$$P_c = \frac{2\sigma}{r} \tag{4.08b}$$

where σ (MT⁻²) is interfacial tension at the gas-water interface, θ is the contact angle and R (L) is the pore radius. Assuming θ is constant in time, $\frac{\cos\theta}{R}$ can be expressed as r (L), which is the effective pore radius, which is treated here as the critical pore radius. The capillary pressure computed for each critical pore radius represents the critical entry pressure, P_e (L), of each grid block to simulate gas invasion (Mumford et al., 2015). Grid blocks were also assigned a terminal pressure, P_t (L), to allow simulation of imbibition of water in pores that could no longer retain gas. Terminal pressures were computed at each pore by the parametric constant, α :

$$\alpha = \frac{P_t}{P_e} \tag{4.09}$$

In a system contaminated with chemical surfactants, the migration and fragmentation of trapped fluids are coupled with solute transport processes. Reductions in interfacial tension will induce a proportional reduction in critical entry and terminal pressures (equation 4.08), influencing pore scale flow phenomena.

4.2.4. Gas mobilization and fragmentation

A porous network was represented by a series of grid blocks representing a small subsection of porous media (Glass et al. 2001; Gerhard & Kueper, 2003). The flow of gas in the MIP-IFT model is comprised of multiple gas and water invasion (drainage and

imbibition) events occurring simultaneously. To capture the combined effects of capillary and buoyant forces on the flow of disconnected gases through a saturated porous medium, critical threshold entry and terminal values were assigned to each grid block:

$$T_e = P_e + P_w \tag{4.10}$$

$$T_t = P_t + P_w \tag{4.11}$$

where T_t (L) is the terminal threshold, and T_e (L) is the entry thresholds. P_w (L) is the hydrostatic pressure, and is incorporated to consider the effects of buoyancy on gas flow, defined as:

$$P_w = \rho_w gh + P_0 \tag{4.12}$$

where ρ_w (ML⁻³) is the density of water, g (LT⁻²) is the acceleration due to gravity, h (L) is the height of water, and P_0 (L) is the pressure at the top of the domain.

For mobilization and fragmentation of a disconnected gas to occur during MIP, a series of conditions must be met. Invasion of gas into a saturated pore will only occur upon exceeding the entry pressure of the neighbouring grid block with the lowest capillary resistance. It is assumed that trapped gas in the MIP-IFT model exhibits constant volume, in which expansion does not contribute to gas migration. As such, when invasion of gas occurs, imbibition must occur simultaneously in another grid block. Typically, this is assumed to occur at the connected, gas-occupied grid block with the highest terminal pressures, which is, consequently, most favourable for invasion by water. Available grid blocks are identified based on grid block connectivity. Gas migration is only possible if both entry and terminal conditions are met. That is, for gas to invade a neighbouring water-occupied block, it must be capable of exceeding the entry threshold

of that block while simultaneously being capable of withdrawing water from a gasoccupied grid block:

$$T_t > T_e^{\min} \tag{4.13}$$

Furthermore, in MIP-IFT, grid blocks are identified not only for maximum terminal and entry pressures, but for proximity of the imbibition site to the favourable gas invasion site:

$$d = \sqrt{(T_{e,x}^{min} - T_{t,x})^2 + (T_{e,z}^{min} - T_{t,z})^2}$$
(4.14)

where d (L) is the Euclidean distance between the grid blocks undergoing gas invasion and imbibition. Previous MIP models have assumed instantaneous pressure redistribution with each mobilization event, in which gas rearranges itself within pore spaces to maintain a uniform gas pressure after transport (Mumford et al., 2009). Gas redistribution results in higher capillary pressures at the top of the gas and lower capillary pressures at the bottom, resulting in the most favourable imbibition sites being near the bottom of gas clusters or gas pools. If this process of pressure redistribution is not instantaneous, reduced capillary pressures at the top of the gas become favourable for imbibition, leading to snap-off and fragmentation of the mobilized gas into disconnected clusters rather than mobilization of gas cluster from the bottom up. Therefore, in this study water is withdrawn from the gas-occupied block nearest to the grid block capable of gas invasion (lowest *d* using equation 4.14) that satisfies equation 4.13.

Mobilization of gas will persist as long as capillary forces at the upper boundary of the gas are continuously exceeded by opposing forces (Roy & Smith, 2007). If the

capillary pressure at the top of the gas overcomes those opposing forces, the pool will terminate at a critical height of:

$$h_{gas} = \frac{P_c^{top} - P_c^{bottom}}{\Delta \rho g}$$
(4.15)

in which h_{gas} (L) is the height of the gas pool, P_c^{top} (L) is the capillary pressure at the top of the gas pool, P_c^{bottom} (L) is the capillary pressure at the bottom of the gas pool, and $\Delta \rho$, is the density difference of the gas and liquid. The critical height of an immobile gas pool after contamination with a chemical surfactant was expressed in this work as the contaminated pool height ratio:

$$H_{F:I} = \frac{H_{Co}}{H_0}$$
(4.16)

where $H_{F:I}$ is the ratio of the final pool height to the initial generated gas pool height, H_{Co} (L) is the height of the gas pool at different stages of contamination with surfactant, and H_0 (L) is the initial height of the gas pool before contamination with surfactant.

In summary, transport of 1-BuOH through the flow-cell would result in the gradual reduction of capillary pressures defining pores at the upper boundary of an entrapped gas pool proportional to the reduction in interfacial tension (Figure 4.2). Gas invasion is initiated if possible, at sites most favourable for gas flow, simultaneous to imbibition. To simulate gas migration behaviours similar to experiments in the presence of 1-BuOH, as gas migrated to the surface of the sand pack, the gas was removed from the top boundary of domain to represent release to the atmosphere. If gas invasion is not possible, gas migration does not occur, and 1-BuOH is transported further through the flow domain.

4.3. Model implementation

4.3.1. Summary of experiments

The MIP-IFT model was used to simulate the effects of a 1-BuOH spill on the behaviour of an immobile gas pool below a capillary barrier based on laboratory flow cell experiments (Chapter 3; Elliott & Smith 2020). Simulations conducted in this study were compared to the flow-cell experiments, in which the height of the gas pool was analyzed at different stages of contamination in both model simulations and the laboratory experiment.

The laboratory experiment was conducted in a two-dimensional flow cell packed with sands to a height of 43.4 cm and a width of 58.8 cm. The flow-cell was confined by two glass plates to a thickness of 1.1 cm in order to isolate the analysis to only twodimensions. The cell was packed with a coarse sand background material and a fine sand capillary barrier designed to optimize gas entrapment for analysis and measurement of gas pool height with contamination of chemical surfactants (Figure 4.3). The capillary barrier can be separated into two components; with a cap 4.2 cm in height and 42.0 cm in length, and arms 14.7 cm in height and 6.0 cm in length.

Dry sand was packed into the flow cell, and initial water-wet conditions were established by rapidly saturating the sand using a constant head method in which high hydraulic flow rates ($8x10^{-6} \text{ m} \cdot \text{s}^{-1}$) would minimize gas generation below the capillary barrier. The flow-cell was then drained and re-saturated to trap gas below the capillary barrier. To generate the gas pool, a low upwards hydraulic gradient was applied to simulate a progressive rise in water table level at a slower hydraulic flow rate ($2x10^{-6} \text{ m} \cdot \text{s}^{-1}$)

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¹), terminating once the capillary fringe had reached the bottom of the arms of the capillary barrier. The partially saturated flow-cell was left to equilibrate over a period of 12 hours, during which capillary rise in the fine sand allowed for its complete saturation, closing an immobile pool of air off from the atmosphere. Once the capillary barrier was completely saturated, the rest of the porous medium was saturated, generating a trapped gas pool extending across the barrier at the critical height of 8.4 ± 0.4 cm.

To contaminate the quasi-saturated system in the flow-cell, 1-BuOH was pooled along the surface of the sand pack to a depth of 3.5 cm. Contaminant migration was initiated through the system once a constant downward hydraulic gradient was applied. Throughout the experiment, the 1-BuOH pool was continuously restored by applying fixed volumes of 1-BuOH to the sand to inhibit source depletion and establish complete contamination of the gas pool over time. Gas migrated through the flow-cell in a series of individual release pathways through the porous medium episodically as 1-BuOH reached the top of the gas pool. Mobilization resulted in a non-linear decrease in gas pool height with time, to a final measured height of 2.7 ± 0.2 cm. Concentration-dependent interfacial tension reductions were assumed to be the primary variable influencing gas flow, in which dynamic contact angle variations were considered negligible in comparison. Similarly, mass transfer of solutes was assumed negligible due to the low vapour pressure of 1-BuOH of 0.91 kPa (Butler et al., 1935) and did not contribute to gas behaviour when contaminated.

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4.3.2. Experimental domain

To simulate 1-BuOH experiments, the MIP-IFT model was implemented in a domain of similar dimensions and features as the flow-cell sand pack (Table 4.1). The domain was 434 mm in height and 588 mm in width. The domain was two-dimensional and characterized by different entry and terminal pressures assigned to each individual grid block. These pressures were established based on the Brooks-Corey soil retention model parameters quantified for the porous materials comprising the capillary barrier and background sand in the flow-cell experiments using the hanging water column method outlined in Chapter 3 Elliott & Smith 2020 (Figure 4.4). The distribution of entry and terminal pressures in the capillary barrier and background is shown in Figure 4.5.

4.3.3. Gas emplacement

The initial gas pool in the model was emplaced below the capillary barrier in the domain based on the pool height measured in the laboratory flow-cell. The average initial gas pool height of 500 simulations was 9.8 ± 0.3 cm, extending across the width of the coarse material below the capillary barrier. Variability between simulations was a result of gas redistribution and parameter rounding in MIP-IFT model, being slightly greater than experimental measurements. The contrasting material properties of the capillary barrier and background sand generated a gas pool with a height dependent on the capillary pressures based on the hydraulic conditions of the system upon trapping (Gerhard & Kueper, 2003). Based on initial wetting conditions established in the flow-cell, the critical pool height created was characteristic of capillary pressures at the top of the pool equal to the terminal pressure of the finer material. Similarly, the capillary pressure at the bottom of the pool was assumed to exist at the terminal pressure of the coarser material. The measured pool height agreed with the assumption that the pool was generated under wetting conditions, based on equation 4.15 and the material properties characterizing the background and capillary barrier sands.

4.3.4. Simulations and model runs

The MIP-IFT simulations were run using a stochastic modelling approach, in which different random distributions of entry pressure were generated to represent sediment variability with each realization. 500 realizations were simulated, which was deemed to be sufficient based on the convergence of the cumulative average and variance of the final gas pool height (Figure A.1). These simulations are referred to as EX1 to EX500 (Table 4.2). Simulated gas pool heights were averaged over the 500 realizations at the critical times based on the decrease in the gas pool height with time during the experiment. In addition to simulations performed to compare simulated results to the results of the experiment (EX1-500), a series of simulations were run to conduct a sensitivity analysis. Sensitivity analysis was conducted in 500 iterations for each model modification, IT1-3, GS1-3, and HY1-3, to ensure an appropriate representation of the statistical population size. Additionally, visual model outputs were produced to qualitatively compare the behaviour of gas under different conditions. EX2 was used for comparison to the different model parameters applied to the same distribution of capillary pressures in the flow domain. Model parameters were modified to analyze MIP-IFT sensitivity to variability in interfacial tension (IT1-3), grain sizes characterizing the capillary barrier (GS1-3), and hysteresis of the sediment characterizing the capillary barrier (HY1-3)
(Table 4.2). As capillary forces are a primary component in driving multiphase flow phenomena, it was hypothesized that one of the primary variables in gas migration in the IFT-MIP model was interfacial tension. The model was modified to analyze the implications of a very strong surfactant with an interfacial tension of 4 mN·m⁻¹ (IT1), and two weaker surfactants with interfacial tension of 55 mN·m⁻¹ and 38 mN·m⁻¹ (IT2 and IT3, respectively). The initial height of the gas pool was the same as for EX1-500. In all scenarios, advective and dispersive transport processes were the same.

The material properties of the capillary barrier characterizing the strength of capillary forces that maintain immobility of a gas pool were hypothesized to have significant impacts on mobilization initiation, migration and termination of gas flow through the porous medium. To analyze the effects of grain size on the migration of gas when contaminated with 1-BuOH, the characteristic entry and terminal pressures of the fine sand in the model were shifted equally to represent a change in grain size, while maintaining sediment sorting. The entry pressures and terminal pressures were increased by 5 cm in simulation GS1 and 10 cm in simulation GS2 to investigate the effects of capillary barriers finer than the original arrangement. In GS3, the terminal and entry pressures were decreased by 5 cm. It was also expected that the behaviour of the gas pool depends on the hysteresis of the material comprising the capillary barrier. The model was modified to exhibit different hysteretic properties by increasing the separation between the main wetting and draining curves of the fine sand composing the capillary barrier (Topp, 1971). While the terminal pressure of the fine sand was unchanged, the critical entry pressure was increased by 5 cm in HY1 and by 10 cm in HY2 to exhibit an increase

in hysteresis. To simulate a decrease in hysteresis, the entry pressures was reduced by 5 cm in HY3.

4.4. Results and discussion

4.4.1. Overview of gas migration

One-dimensional infiltration of 1-BuOH through a quasi-saturated system over time resulted in the mobilization of an immobile gas pool trapped beneath a fine sand capillary barrier in both model simulations and the laboratory flow-cell experiment (Figure 4.6). Simulated contaminant breakthrough curves generated at critical times during mobilization show the migration of the aqueous 1-BuOH front through the domain with time (Figure 4.6.e). As 1-BuOH concentrations increased with time as infiltration continued, interfacial decreased non-linearly. In the simulations, hydrodynamic dispersion brought low 1-BuOH concentrations to the upper boundary of the gas pool after 29 minutes of infiltration. At this time, the relative concentration of aqueous 1-BuOH at the top of the gas was 0.3%, and the interfacial tension at the gas-water interface was reduced by 1.5 mN·m⁻¹ from that of uncontaminated water. A proportional reduction in entry pressures along the upper boundary of the gas pool triggered the initiation of gas invasion to connected pores (Figure 4.6.b-d). Gas invaded the largest connected pore in the capillary barrier, characterized by the lowest entry pressures along the boundary. opening up an accessible pathway for gas flow. The small reduction in entry pressures required to trigger gas invasion into the capillary barrier provides insight on the capillary pressures defining the porous medium prior to contamination, in which the gas pool was

near its critical threshold height defined by the entry and terminal pressures along the pool boundaries. Gas invasion at the upper boundary was accompanied by simultaneous imbibition at the lower boundary of the gas pool and a decrease in gas pool height with time, as occurred in the experiment (Figure 4.6a).

Connected pores at shallower depths were favourable for gas invasion due to lower hydrostatic pressures and reduced entry pressures of contaminated grid blocks, establishing a continuous gas release path or finger. However, fragmentation of gas caused by snap-off at the top of the capillary barrier would temporarily terminate gas migration through the developed fingers. Therefore, gas release through the capillary barrier in the simulations occurred as a series of episodic escape events, as observed in experiments. To sustain migration of gas through the capillary barrier, further reductions of entry pressures at the upper boundary of the gas pool were required, created by increased concentrations of aqueous 1-BuOH as it migrated deeper in the domain. The arrival of higher 1-BuOH concentrations at the upper boundary of the gas and further reduced entry pressures of pores along the capillary barrier with time would increase the number of sites available for gas invasion. Smaller pores with high entry pressures previously unfavourable for invasion would become available for displacement by gas as entry pressures were reduced proportionally to reduced interfacial tensions (Equation 4.08). More pathways available for gas flow at higher contaminant concentrations were observed in flow-cell experiments and simulated in the model as increased escape paths or fingers through the capillary barrier (Figure 4.6.c).

Gas migration terminated in all simulations at a critical pool height as high concentrations of aqueous 1-BuOH no longer facilitated a further reduction in interfacial tension and entry pressures along the upper boundary of the gas pool (Figure 4.6e). The final average gas pool height based on the 500 realizations was 4.1 ± 0.8 cm (Figure A.2). The final gas pool height measured in the laboratory experiment was 2.7 ± 0.2 cm with a contaminated pool height ratio of 0.32 ± 0.03 (Table 4.3). The contaminated pool height ratio captured the behaviour of the experiment with a value of 0.39 ± 0.08 . The final gas pool height is characterized by the capillary pressures defining the contaminated medium (Equation 4.15). The contaminated pool height ratio can be directly related to the reduction in interfacial tension from contamination with a chemical surfactant. Equation 4.15 can be modified to consider a contaminated interface by incorporating the ratio of interfacial tension of a surfactant-air interface to a water-air interface:

$$h_{gas} = \frac{\left(P_c^{top} - P_c^{bottom}\right)\left(\frac{\sigma_s}{\sigma_w}\right)}{\Delta\rho g} \tag{4.17}$$

where σ_s (ML⁻²T⁻²), is the interfacial tension of the surfactant contaminated interface. The ratio of the interfacial tension of 1-BuOH-air to water-air is, 0.33, similar to that of the contaminated pool height ratio simulated in the model and experiment.

Using the MIP-IFT model, they key aspects of the experiment were recreated (Figure 4.7). The gas pool decreased in height non-linearly with time in the simulations, capturing the behaviour observed in the experiment. The variability in gas release rate and pool height demonstrated in 50 (of 500) model realizations shown in Figure 4.7 emphasizes the complex nature of multiphase flow through porous media, and the effects of pore-scale variability on transport and disconnected gas flow.

4.4.2. Mechanisms driving initiation and termination

Mobilization of a trapped gas pool is initiated as the capillary pressures at the upper boundary of the gas pool exceed the entry pressures of connected pores in the capillary barrier. In other words, mobilization of gas is triggered once buoyant forces of gas overcome retaining capillary forces. Contamination of the porous medium by chemical surfactants results in the reduction in capillary forces proportionally to the decrease in interfacial tension. Arrival of aqueous 1-BuOH at the top of the gas pool allowed buoyant forces to exceed the weakened capillary forces, initiating the upwards flow of gas. Gas migration would be sustained as long as buoyant forces continued to exceed capillary forces, and imbibition was possible at the bottom of the pool. As mobilization can only persist if Tt^{max} exceeds Te^{min}, increased concentrations of 1-BuOH at the top of the gas pool allowed for the continuous release of gas by continuous reduction in entry pressures along the capillary barrier. Gas migration was temporarily terminated when Tt^{max} no longer exceeded the reduced entry pressures at the upper gas pool boundary. Early in time, the decrease in gas pool height was directly dependent on the interfacial tension at the upper boundary of the gas pool (Figure 4.8).

Termination of gas migration was the result of two summative processes: reduced buoyant forces of smaller gas pool and weakened terminal pressures of a contaminated system at the lower boundary of the gas. In both model simulations and laboratory experiments, a decrease in gas pool height and volume below the capillary barrier resulted from gas release. Reduced buoyant forces of a smaller gas pool limits the ability to overcome weakened capillary forces, resulting in a decrease in gas released with time,

despite further decrease in interfacial tension at the top of the gas (Figure 4.8). As the gas pool decreased in height, the terminal thresholds at the bottom of the pool were reduced due to the decrease in hydrostatic pressures with depth. As 1-BuOH migration through the porous medium was maintained throughout the simulation, arrival of the contaminant front at the bottom of the gas pool would induce a decrease in terminal pressures and thresholds defining the pores across the lower boundary. The effects of this can be observed in Figure 4.8, in which the rate of gas release plateaus despite further reductions in interfacial tension at the upper boundary of the pool. As the capillary forces at the bottom of the pool weaken upon contamination, the ability to induce imbibition of gas filled pores reduces, and fewer blocks are available for T_t^{max} to exceed T_e^{min} . In summary, as mobilization continues later in time, gas release through the capillary barrier becomes less favourable due to a reduced terminal threshold at the lower boundary of the pool as hydrostatic pressures and terminal pressures are reduced with smaller pool heights and contamination respectively. Mobilization terminates when the gas pool establishes a new critical height, in which the smaller, contaminated displacement pressure can no longer be exceeded. In other words, the capillary pressures at the bottom of the pool are unable to exceed the displacement pressure of the contaminated capillary barrier (Gerhard & Kueper, 2003).

4.4.3. Sensitivity analysis

4.4.3.1. Sensitivity to interfacial tension

Gas flow through the porous medium responded differently when contaminated with representative surfactants of different strengths than when contaminated with 1-BuOH in EX3 (Figure 4.9). The same concentration breakthrough curves were generated with each surfactant, however, unique interfacial tension changes with depth resulted from the application of different surfactants. Mobilization was initiated at different times in IT1-3 based on the strength of the chemical surfactant applied, despite the same concentration at the upper boundary of the gas pool. After 29 minutes of infiltration of the strongest surfactant in IT1, the contaminated pool height ratio had reduced to 0.67 at an interfacial tension of 69.2 mN·m⁻¹. At this time, gas flow had already been initiated, breaking through the capillary barrier after only 20 minutes of infiltration. In simulation IT2, interfacial tension reductions of a weaker surfactant at the upper boundary were minimal. After 29 minutes of contaminant infiltration, interfacial tension was only reduced to 72.5 mN·m⁻¹, in which no change in gas distribution was observed. Gas migration occurred as a redistribution of the gas pool into connected grid blocks, as the interfacial tension was reduced to 71.9 mN·m⁻¹ after 39 minutes of infiltration. However, gas did not break through the capillary barrier, remaining disconnected and immobile throughout the entire simulation. The volume of the gas did not change, and no gas escaped from the flow domain. In simulation IT3, infiltration of a slightly stronger surfactant would generate gas flow after 41 minutes upon reduction in interfacial tension at the upper boundary of the gas to 68.4 mN \cdot m⁻¹. When an immobile gas pool is contaminated with strong surfactants, large decreases in interfacial tension at low concentrations results in a proportional decrease in entry pressures and capillary forces retaining the gas in place. As contaminant transport processes were unchanged, mobilization was triggered earlier in IT1, as considerable reductions in entry pressures at the upper boundary of the gas pool

resulted from low concentrations of surfactant. A wide range of grid blocks became available for gas invasion as multiple sites are easily exceeded by buoyant forces (Equation 4.8). In contrast, weaker surfactants require higher concentrations to induce a considerable change in interfacial tension from that of a clean interface.

Gas migration terminated at pool heights characteristic of the contaminated porous medium pressure distribution (Figure 4.9). In simulation IT1, migration was terminated after 184 minutes. The final contaminated pool height ratio was 0.02. In contrast, when contaminated with a very weak surfactant in IT2, the pool height remained unchanged throughout the entire model run. Reduction in gas pool height in IT3 was minimal, terminating at a contaminated pool height ratio of 0.73. The difference in gas behaviour when contaminated with different chemical surfactants can be attributed to the extent of interfacial tension reduction established at the bottom of the gas pool upon the arrival of the contaminant front at the lower boundary of the pool. When contaminated with a strong surfactant, such as in IT1, mobilization only slowed once the contaminant front reached the lower boundary of the gas pool. Large reductions in terminal pressures proportional to sharp reductions in interfacial tension at the lower boundary resulted in the immediate termination of gas flow, as imbibition was no longer favourable at any site along the bottom of the pool. In addition to weakened terminal pressures, buoyant forces of a smaller gas pool were too weak to overcome entry pressures along the capillary barrier. The average contaminated pool height ratio of 500 simulations when contaminated with a strong surfactant, was 0.016 ± 0.007 (Figure 4.10). Based on Equation 4.17., the theoretical contaminated pool height ratio when interfacial tensions

are reduced to 4 mN·m⁻¹ is 0.06 (Table 4.2). The difference in theoretical and simulated results are a product of a model limitation, in which the theoretical gas pool height is smaller than the height of a single grid block. The average contaminated pool height ratio of 500 IT3 simulations, was 0.6 ± 0.1 (Figure 4.10). These simulations agree with the theoretical contaminated pool height ratio of 0.52, with variability resulting from differences in the pressure fields generated with each simulation or flow cell packing arrangement (Table 4.2). In IT2, the reductions in interfacial tension and capillary forces at the upper boundary of the gas pool were insufficient to be overcome by buoyant forces, and mobilization did not occur. Once the top pore interfaces had been weakened, migration was no longer favourable, as the contaminant front had reached the bottom of the pool causing a consequential reduction in terminal pressures. Despite reduced entry pressures at the upper boundary of the gas pool, no sites were favourable for imbibition. Gas flow cannot occur if gas is not also simultaneously displaced by water, as expressed by Equation 4.8. However, mobilization did occur in other simulations, resulting in an average contaminated pool height ratio of 0.9 ± 0.1 , in agreement with the theoretical contaminated pool height ratio of 0.8 (Figure 4.10; Table 4.2).

The rate of gas release and flow through the porous medium responded directly to interfacial tension reductions in the presence of different chemical surfactants (Figure 4.11). When contaminated with a very strong surfactant such as in IT1, gas pool height decreased rapidly with time, following a similar trend to the reduction in interfacial tension at the upper boundary of the gas pool. A similar trend was observed in all other simulations, including contamination with 1-BuOH, in which the rate of gas pool height

decrease was similar to that of the rate of interfacial tension decrease at the upper boundary of the gas pool. When snap-off disconnected finger paths from the gas pool, mobilization was immediately initiated, as further reductions in entry pressures would facilitate migration of gas once again. In IT1, large reductions in interfacial tension at the upper boundary of the gas pool occurred prior to any contamination at the lower boundary of the gas pool. As a result, despite reduced gas pool height and buoyant forces, mobilization remained favourable, releasing rapidly through the capillary barrier. In IT2 and IT3, contamination with weaker surfactants exhibited slow migration of gas, as entry pressures were gradually overcome with small reductions interfacial tension. Upon fragmentation of gas, re-mobilization could not occur until further reductions in interfacial tension were induced at the upper boundary of the pool. Gas release in these simulations was limited by high entry pressures of the capillary barrier. Arrival of the contaminant front at the lower boundary further limited imbibition and gas flow through the capillary barrier. In summary, the decrease in interfacial tension induced by surfactants at the gas-fluid interface of the trapped pool directly affected the migration and termination of the non-wetting fluid.

4.4.3.2. Sensitivity to grain size characterizing the capillary barrier

The distribution and flow of gas behaved differently when the grain sizes of the capillary barrier were altered to represent finer and coarser material properties, with unique responses to 1-BuOH contamination (Figure 4.12). The initiation of gas migration in fine sands represented by GS1 and GS2 simulations did not occur until higher concentrations of 1-BuOH arrived at the upper boundary of the gas pool. In simulation GS1, mobilization was initiated after 48 minutes of contaminant infiltration, in which interfacial tensions at the upper boundary of the gas pool were reduced to 56.4 mN·m⁻¹. Gas migrated through several fingers entering the capillary barrier, however, gas escaped to the top of the flow domain through one finger at the edge of the capillary barrier. In GS2, mobilization was initiated through a single finger at the edge of the capillary barrier after 73 minutes, in which interfacial tensions at the upper boundary of the gas pool were reduced to 39.5 mN·m⁻¹. In a coarser material, represented by GS3, mobilization of gas occurred immediately within the first time step, prior to contamination by 1-BuOH. Multiple fingers were generated at sites along the capillary barrier, releasing gas through three main pathways to the top of the flow domain. Several sites were available for gas invasion immediately as entry pressures of a coarse material were low, and easily exceeded by buoyant forces of the gas pool at its initial emplaced height. Additionally, terminal pressures at the lower boundary of the gas pool remained unchanged and were favourable for sustained imbibition throughout gas flow. Multiple gas finger pathways were generated at multiple sites throughout the capillary barrier due to reduced entry pressures characteristic of coarser grained sediments. In contrast, initiation of gas migration in fine sediments represented by GS2 and GS3, capillary pressures must be reduced to a critical threshold in which terminal thresholds at the bottom of the pool can overcome entry thresholds at the upper boundary. The finer sediments composing the capillary barrier required larger reductions in interfacial tension to reduce entry pressures enough to overcome retaining capillary forces and trigger mobilization. Few sites were favourable for invasion of gas in GS2, as high entry pressures across the capillary barrier

limited gas migration and the generation of fingers. Further increases in concentration were required to maintain mobilization through one primary release pathway in both GS1 and GS2.

Gas migration was terminated in all experiments based on the capillary pressure distribution of the contaminated system (Figure 4.12). In simulation GS1, gas migration terminated at an average contaminated pool height ratio of 0.55 ± 0.08 for 500 iterations, in agreement with the theoretical contaminated pool height ratio of 0.47 (Figure 4.10; Table 4.2). Similarly, mobilization in GS2 was short lived, terminating at a contaminated pool height ratio of 0.68 ± 0.08 , also within error of the theoretical contaminated pool height ratio of 0.62. Gas migration in GS3 was only terminated once the contaminant front reached the lower boundary of the gas pool, causing a decrease in the rate of gas flow after 52 minutes. The average contaminated pool height ratio of the final to initial pool height after 500 simulations with reduced entry and terminal pressures was 0.17 ± 0.08 for the coarse material. The theoretical final contaminated pool height ratio based on the reduced capillary pressures using Equation 4.17 was 0.2, agreeing with the simulated results (Figure 4.10; Table 4.2). Mobilization was sustained in GS3 by initially low entry pressures and further reduced capillary forces by 1-BuOH contamination, despite reduced buoyant forces of a smaller gas pool. Gas migration would be sustained until the arrival of the aqueous 1-BuOH front at the lower boundary of the pool. Once the bottom of the gas was contaminated, sites available for imbibition were limited due to reduced terminal pressures, and gas migration could no longer continue. In contrast, mobilization was short lived in GS1 and GS2, as once high enough concentrations

reached the upper boundary to induce mobilization, the contaminant front had already arrived at the lower boundary of the gas pool (Figure 4.13). As a result, gas migration had slowed, leading to termination gas flow at a larger pool height.

As the terminal pressures of the sands were also modified in these simulations, the uniformity of the material remained unchanged, limiting the variability in pore size distribution across the capillary barrier (Table 4.2). The standard deviation of the contaminated pool height ratio of each scenario based on 500 simulations was 0.08. As each material was represented in the model to remain uniform without change in pore size distribution, the final gas pools generated were reproducible, despite unique pressure fields or variability in sediment deposition. These results provide further evidence to support Equation 4.17 and emphasize the importance of grain size distribution and material uniformity on gas entrapment and mobilization. The difference in material properties between layers in contaminated systems can be considered a controlling factor in the generation and stability of trapped non-wetting fluids.

4.4.3.3. Sensitivity to hysteresis of sediments comprising the capillary barrier

As the entry pressures characterizing the materials were modified in each simulation, migration of gas in response to contamination by aqueous 1-BuOH exhibited unique flow behaviour through the porous medium. Unlike flow through a uniform porous medium, gas migration was affected by hysteresis in materials with a wider range of sediment sizes (Figure 4.14). In material characterized by high hysteresis, such as HY1, mobilization was initiated when interfacial tension was reduced to 59.4 mN·m⁻¹ at the top of the gas pool, in which gas migrated through a single finger pathway through the capillary barrier.

Throughout gas migration through the capillary barrier, higher concentrations of aqueous 1-BuOH were not required to maintain flow, as the migration of gas was continuous through the established finger. Complete mobilization occurred in one time step. This same behaviour was observed in HY2. Although requiring an interfacial tension of 48.3 mN·m⁻¹ to initiate mobilization, migration occurred through a single pathway and was continuous through the capillary barrier. Snap-off was observed at the top of the capillary barrier in the coarse material only. Migration through a capillary barrier with limited hysteresis in HY3 demonstrated numerous snap-off events throughout migration, resulting in a discontinuous flow of gas through the porous medium. Low initial entry pressures characterizing the capillary barrier in HY3 allowed mobilization immediately, prior to contamination with aqueous 1-BuOH. However, flow was discontinuous throughout the capillary barrier, in which gas pathways became disconnected in several sites through the material. Higher concentrations of aqueous 1-BuOH were required to maintain migration through the material, as gas was constantly being disconnected. Less hysteresis in the capillary barrier quantified by minimal difference between terminal and entry pressures defining the pore spaces increased the favourability for snap-off within the material. Multiple sites were available for imbibition, as terminal pressures readily exceeded reduced entry pressures of the invaded grid blocks, while maintaining close proximity to invasion sites in the capillary barrier. In contrast, fewer sites in the trapping layer were favourable for fragmentation and snap-off in HY1 and HY2. Gas release was continuous as the increased critical entry pressures increased the difference between terminal and entry pressures defining the medium. Fewer sites in the layer were

favourable for imbibition and thus fragmentation, as few pores had terminal pressures capable of exceeding entry pressures near invasion sites. As a result, gas release was continuous, without the need for further reductions in interfacial tension to maintain gas flow.

Gas migration was terminated at unique heights characteristic of the porous medium properties (Table 4.2). Gas migration of 500 simulations in HY1 and HY2 were terminated at an average contaminated pool height ratio of 0.4 ± 0.1 and 0.5 ± 0.1 respectively. These results are within error of the theoretical contaminated pool height ratios based on the modified entry and terminal pressures of a contaminated system. In contrast, the average results of 500 simulations of HY3 did not agree with the theoretical contaminated pool height ratio of 0.17, with a simulated model average of 0.25 ± 0.04 . In simulations HY1 and HY2, reduced fragmentation limited termination of gas flow, as mobilization remained favourable as the connected finger extended to shallower depths in the flow domain. Reduced entry thresholds at a shallower depth, due to reduced hydrostatic pressures, were easily exceeded by terminal thresholds at the bottom of the gas pool without further reductions in interfacial tension (Figure 4.15). Termination of gas only occurred as the lower boundary of the gas pool became contaminated, reducing terminal thresholds to limit exceedance of entry pressures of the extended finger. High hysteresis can result from arrangement and distribution of pores and pore throats in a porous medium, often accompanied with increased variability in pore size distribution. High variability in pore size distribution resulting in reduced sediment uniformity leads to greater variability in final pool heights, as indicated with higher standard deviations for

HY1 and HY2. In contrast, continuous fragmentation of gas in HY3 limited connected gas flow paths through the capillary layer, resulting in premature termination of the pool. Continuous contamination of the gas pool was required to reconnect fingers separated by fragmentation. Few transport steps were conducted with each time step as the contaminant front migrated through the domain, demonstrated as a gradual reduction in pool height with time (Figure 4.15). Arrival of the aqueous 1-BuOH front at the lower boundary of the gas pool would inhibit further gas flow, resulting in premature termination of flow. Reduced hysteresis effects characteristic of more uniform materials resulted in reduced variability in final pool height as indicated by lower standard deviations in HY3 (Table 4.2). The hysteretic properties of a porous media directly affect the behaviour and variability of gas flow through saturated sediments. The hysteretic and material properties of the trapping layer impacted the behaviour and migration of gas throughout mobilization by introducing variability in snap-off mechanisms and fragmentation throughout the material. Additionally, reduced uniformity of the fine layer limits the predictive power of Equation 4.17, as variability increases with reduced sediment sorting.

4.5. Conclusion

The MIP-IFT model was developed to simulate the effects of concentration dependent interfacial tension of an aqueous 1-BuOH contaminant front on a trapped gas pool below a capillary barrier. The model was validated against flow-cell experiments with the same sand packing arrangement and sediment properties based on observations of gas mobilization and termination. One-dimensional advective-dispersive transport of aqueous 1-BuOH through the flow domain resulted in the initiation of gas migration through a confining capillary barrier by reducing entry pressures proportional to the reduction in interfacial tension induced by the surfactant. Gas migration was initiated at the same time as the laboratory flow-cell experiments, releasing episodically through multiple finger paths through the capillary barrier as the concentration of 1-BuOH increased at the upper boundary of the pool. Gas flow was maintained as buoyant forces of the gas pool were able to overcome weakened capillary forces of a contaminated porous medium. However, gas flow was only sustained if the buoyant forces continuously exceeded capillary forces. Gas migration was terminated due to the summative effects of reduced buoyant forces of a smaller gas pool and limited imbibition due to a contaminated lower boundary of the gas pool. Migration of gas terminated at an average contaminated gas pool height ratio of 500 model simulations of 0.39±0.08, within error of the measured ratio in the experiment of 0.32 ± 0.03 . The contaminated gas pool height was proportional to the reduction in interfacial tension induced by the chemical surfactant, 1-BuOH.

A sensitivity analysis was performed using the MIP-IFT model to further understand the primary components effecting mobilization and flow of immobile gas in contaminated groundwater systems. The effects of porous media properties on gas migration in response to contamination were analyzed by changing sediment grain size and hysteretic properties of the capillary barrier. Increasing critical entry and terminal pressures defining the capillary barrier of the flow domain by 5 and 10 cm limited gas

transport, despite contamination with 1-BuOH, terminating at a larger gas pool with a contaminated pool height ratio of 0.55±0.08 and 0.68±0.08 respectively. By reducing entry and terminal pressures by 5 cm, gas flow through the capillary barrier was favourable, terminating at a smaller gas pool with a contaminated pool height ratio of 0.17 ± 0.08 . Similarly, the behaviour of gas through the capillary barrier is affected by the hysteretic properties that define the material comprising the confining layer. A capillary barrier defined by high hysteresis results in a wider variability in final gas pool height, as even small variabilities in pore distribution can influence the migration of gas through a medium. Reduced fragmentation in these materials resulted in continuous gas flow to gas pool heights smaller than expected. Materials characterized by high hysteresis demonstrate greater fragmentation and larger gas pools due to premature termination. Furthermore, the model demonstrated a sensitivity to chemical surfactants of different strengths on the flow of gas through the porous medium. Contamination with a very strong chemical surfactant characterized by an interfacial tension of 4mN·m⁻¹ terminated gas migration at a contaminated pool height ratio of 0.016±0.007 as buoyant forces were able to easily overcome weakened capillary forces. Contamination with weaker surfactants demonstrated contrasting results, in which gas migration terminated at larger gas pool heights. Reducing interfacial tension to 55 and 38 mN·m⁻¹ terminated at a contaminated gas pool height ratio of 0.9 ± 0.1 and 0.6 ± 0.1 respectively. The model simulations displayed a direct quantifiable relationship between interfacial tension and reduction in gas pool height, in which the final contaminated pool height ratio was

proportional to the relative decrease in interfacial tension induced by the chemical surfactant.

The MIP-IFT model was able to capture the behaviours and key mechanisms of gas mobilization caused by contamination with 1-Butanol based on hydrogeologic and contaminant properties extracted from a laboratory experiment. However, to capture the behaviours observed in the flow-cell experiment, the pore-size distribution parameter (λ) from the Brooks-Corey curves was modified to allow effective use of the inverse transform sampling method to assign representative capillary pressures to the domain. The measured λ parameter representative of the less uniform material was not able to reproduce experimental results using this method, at the resolution applied. Future work in developing a method for grid block resolution in IP models would approve upon the ability to simulate multiphase phenomena in physical experiments and natural systems. This work demonstrated the limitations of the inverse transform sampling method, in which the technique is constrained to uniform porous media.

The impacts of modern biofuel contaminants on quasi-saturated groundwater systems is limited in the literature. The surfactant properties that influence the chemical and physical interactions of these compounds has the capacity to alter natural systems containing trapped gases and other residual non-wetting fluids, by triggering mobilization. This model was able to capture key mechanisms controlling trapped gas migration upon contamination of a chemical surfactant, providing insight on complex multiphase flow phenomena in different geological settings. Further work may apply the theories developed from this study to model the migration of trapped dense non-aqueous phase liquids through saturated media. This model was able to capture the behaviours demonstrated in a constrained laboratory setting. Future work may also use this model to simulate multiphase non-wetting fluid flow in natural porous media, to further analyze the effects of concentration dependent interfacial tension on the mobilization, migration and termination of immobile fluids trapped within pore spaces.

4.6. Figures and tables



Figure 4.1. *Concentration- interfacial tension relationship of 1-butanol* (Smith, J. E., & Gillham, R. W. 1999).



Figure 4.2. *Conceptual model of the IFT-MIP algorithm*. The model can be represented as a loop, in which the transition to a new time step represents the next mass transport step. Upon mobilization initiating, the next time step was not prompted until no available invasion sites were identified.



Figure 4.3. *Flow-cell apparatus and sand packing dimensions*. Sand packing arrangements for aqueous and 1-BuOH contamination, where dark grey material represents Opta 56.3.10 fine sand, light grey is GS-20 coarse sand, and white dotted is B.P.T18.7 coarse sand.

Parameter	Description	Value					
Porous media properties							
P_c^e , P_c^t	Entry pressure and terminal pressure of coarse 10.36, 4.70						
	sand (cm)						
P_f^e , P_f^t	Entry pressure and terminal pressure of fine	20.92, 12.80					
	sand (cm)						
α_c, α_f	Pe/Pt ratio of fine and coarse sand (-)	2.20, 1.63					
λ_c, λ_f	Brooks-Corey pore size distribution index of	4.69, 3.02					
-	fine and coarse sand (-)						
Fluid properties							
$ ho_w$	Density of water $(kg \cdot m^{-3})$ 1000						
g	Gravitational constant (m·s ⁻²)	9.81					
σ_w	Interfacial tension of air-water (mN·m ⁻²)	72					
Mass trans	port properties						
D_d	Molecular diffusion coefficient (m ² ·s ⁻¹) ^a	9.60×10^{-10}					
ω	Tortuosity coefficient (-) ^b	0.7					
\bar{v}	Linear pore water velocity (m/s) 2.05×10^{-5}						
h_{pool}	Initial LNAPL depth (mm)	35					
Interfacial	tension properties						
<i>C</i> ₀	Initial relative concentration of 1-BuOH (%)	100					
a, b	1-BuOH specific constants (-) ^c 0.00365, 0.215						
Numerical parameters							
nt	Time step (minutes)	800					
L_h, L_w	Height and width of flow cell domain (mm)	434, 588					
C_h, C_w	Height and width of capillary barrier cap (mm)	43, 420					
LA_h , LA_w	Height and width of capillary barrier left arm	147, 60					
	(mm)						
RA_h, RA_w	Height and width of capillary barrier right arm	147, 60					
	(mm)						
h _{gas}	Initial thickness of gas pool (mm)	84					
dh, dw	Horizontal and vertical grid spacing (mm)	10, 10					
Boundary conditions							
P _{top}	Pressure at surface of the flow cell (cm)	0					
	L ' (D C 100C						

Table 4.1. Input variables used in MIP-IFT model.

a. Hao, L., & Leaist, D. G. 1996.

b. Fetter, C. W., et al. 1999.

c. Smith, J.E., & Gillham, R. W. 1999.



Figure 4.4. *Brooks-Corey model capillary pressure-saturation relationship curves for coarse sand and fine sand.* The Brooks-Corey models were generated for both drainage and wetting curves to represent both materials used in laboratory experiments to apply to the MIP-IFT model. The red solid line and red dashed line represent the wetting and draining curves respectively for the GS-20 coarse silica sand. The blue solid line and blue dashed line represent the wetting and draining curves of the Opta-56 fine silica sand respectively.



Figure 4.5. *Initial pressure field generated for the model based on inverse transform sampling of Brooks-Corey curves.* The spatial distribution of the entry pressures (a) and terminal pressures (b) were generated based on the capillary pressure-saturation curves of the sand materials, represented as a green colour gradient. The LNAPL contaminated zone can be observed at the top of the domain, displaying a region of reduced pressures. The spatial distribution of entry (c) and (d) terminal thresholds introducing the summation of hydrostatic pressures and capillary pressures can be observed in pink.

Simulation	Description	Variable	Contaminated pool				
		modification	neight ratio (H _{F:I})				
EX1-500	Experimental parameters;	$P_f^e = 20.92$	0.39				
	average of 500 realizations	$P_{f}^{t} = 12.80$					
		a = 0.00365					
Surfactant interfacial tension properties:							
IT1	Stronger surfactant, reducing	a = 0.001	0.06				
	interfacial tension to 4 $\text{mN}\cdot\text{m}^{-1}$						
IT2	Weaker surfactant, reducing	a = 0.0365	0.76				
	interfacial tension to 55						
	mN·m ⁻¹						
IT3	Weaker surfactant, reducing	a = 0.01	0.52				
	interfacial tension to 38						
	$\mathbf{mN}\cdot\mathbf{m}^{-1}$						
Capillary ba	arrier material: grain size proj	perties					
GS1	Finer sand, well-sorted	$P_{f}^{e} = 25.92$	0.47				
		$P_f^t = 17.80$					
GS2	Finer sand, well-sorted	$P_f^e = 30.92$	0.62				
		$P_{f}^{t} = 22.80$					
GS3	Coarser sand, well-sorted	$P_f^e = 15.92$	0.17				
		$P_{f}^{t} = 7.80$					
Capillary barrier material: hysteresis							
HY1	Finer sand, poorly sorted	$P_f^e = 25.92$	0.47				
HY2	Finer sand, very poorly sorted	$P_f^e = 30.92$	0.62				
HY3	Coarser sand, very well sorted	$P_f^e = 15.92$	0.17				

 Table 4.2. Sensitivity analysis model modifications and theoretical gas pool height.



Figure 4.6. *Mobilization of gas and decrease in pool height with increased concentrations of 1-BuOH*. Decrease in gas pool height with increased concentration over time in (a) flow-cell experiments and (b, c, d) model simulations of gas migration in response to 1-BuOH contamination, along with contaminant breakthrough curves and the corresponding interfacial tension with time through the flow-cell domain (e).

Table 4.3. Gas pool height decrease of as a result of surficial contamination of 1-BuOH at the gas-water interface (pool height ± standard deviation). Simulated average of 500 model realizations.

Time (minutes)	1	29	32	36	200
Final measured gas	8.5 <u>±</u> 0.4	8.5 <u>+</u> 0.4	6.4 <u>+</u> 0.3	4.3±0.2	2.7 <u>±</u> 0.2
pool height					
<i>experiment</i> (cm)					
Final average gas	9.8 ± 0.3	9.1 <u>±</u> 0.9	9 <u>±</u> 1	8 <u>±</u> 1	4.1 ± 0.8
pool height					
simulation (cm)					
Measured	1.00±0.09	1.00 <u>+</u> 0.09	0.75 <u>±</u> 0.07	0.51 <u>±</u> 0.05	0.32 ± 0.03
contaminated pool					
height ratio (H _{F:I})					
experiment					
Average	0.98 ± 0.02	0.9 ± 0.1	0.9 <u>±</u> 0.1	0.8 ± 0.1	0.39 ± 0.08
contaminated pool					
height ratio (H _{F:I})					
simulation					



Figure 4.7. *Contaminated pool height ratio with time*. contaminated pool height ratio of 50 model simulations with time (dotted-grey) and the measured contaminated gas pool height ratio of the flow-cell experiment in response to 1-BuOH contamination (red).



Figure 4.8. *Interfacial tension and average gas pool height with time.* Interfacial tension at the upper boundary of the gas pool (red) and lower boundary of the gas pool (blue) decreased non-linearly with time as the contamination front migrated through the flow cell. Average contaminated pool height ratio of 500 simulations decreased non-linearly with time (black-dotted line).



Figure 4.9. *Migration of gas with increased concentration of contaminants with variable surfactant strengths over time (IT1, IT2, IT3)*. Model simulations of gas migration in response to contamination alongside respective contaminant breakthrough curve and corresponding interfacial tension change with time through the flow-cell domain.



Figure 4.10. Bar chart representation of the average contaminated pool height ratio of 500 model realizations for each modification.



Figure 4.11. (a) *Contaminated pool height ratio with time;* **(b)** *modified interfacial tension of each simulation with time.* Simulation IT1 (green) depicts strongest surfactant, simulation IT2 (yellow) and IT3 (red) are weak surfactants compared to original simulation EX2 (blue).



Figure 4.12. Model simulations of migration of gas with capillary barriers of different grain sizes over time (GS1, GS2, GS3).



Figure 4.13. *Model simulation of the contaminated pool height ratio over time with capillary barriers of different grain size.* Simulation GS1 (red) and GS2 (yellow) depict fine sands, and GS3 (green) coarser capillary barrier material compared to original simulation EX2 (blue).



Figure 4.14. Model simulations of migration of gas with capillary barriers of different hysteretic behaviours over time (HY1, HY2, HY3).



Figure 4.15. *Model simulation of the contaminated pool height ratio over time in different hysteretic porous media.* Simulation HY1 (red) and HY2 (yellow) depict highly hysteretic materials, and HY3 (green) minimal hysteresis in the capillary barrier material compared to original simulation EX2 (blue).
4.7. References

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Chapter 5: Conclusions and Future Work

As the demand for gasoline and fuel alternatives continues to rise in a changing environment, the development and advancement of biofuel technology persists. As with any fuel or oil resource, contamination and spill events are inevitable. In order to continuously develop and enhance modern remediation technologies, a complete understanding of the behaviour and interactions that take place with emerging contaminants in nature is critical. The appearance of new chemical constituents to groundwater requires thorough investigation and understanding of contaminant fate and transport. Although biofuels present an opportunity to reduce and limit greenhouse gas and carbon emissions to the atmosphere, the consequences and potential adverse effects associated with the technology are critical to understand prior to application on a global scale. This research focused on understanding the effects and interactions that take place with modern biofuel additives; ethanol, 1-butanol, tertiary butanol, and iso-butanol, from fuel spills in quasi-saturated groundwater systems.

This work demonstrated the effects of modern biofuel additives on the mobilization and migration of trapped gases in a quasi-saturated porous medium, through a series of laboratory experiments. Fundamental concepts and relationships were developed to demonstrate the effects of interfacial tension on migration and termination of trapped gas through an initially saturated porous medium. Experiments conducted displayed a direct relationship between interfacial tension and the terminal height of a gas pool, agreeing with the hypothesis, in which the reduction in the height of a gas pool contaminated with biofuel additives will be proportional to the reduction in interfacial

tension induced at the air-fluid interface. Contamination of an immobile gas pool with biofuel additives results in the initiation of gas migration through a porous medium as the capillary forces keeping a trapped fluid immobile are weakened. Entry pressures of connected pores are reduced proportionally to the reduction in interfacial tension induced by a chemical surfactant, or biofuel additive. Continuous infiltration of aqueous biofuel additives through a quasi-saturated system facilitates the migration of gas through the porous medium, causing a decrease in gas pool height with time, until terminating at a gas pool height characteristic of the contaminated material properties. Gas flow terminates as a result of two summative processes: reduced buoyant forces of a reduced gas pool height and limited imbibition sites available due to a reduction in terminal pressures. Under these conditions, the reduction in gas pool height of a contaminated system is proportional to reduction in interfacial tension induced by the applied chemical surfactant.

Further analyses provided insight on the effects of different hydraulic conditions and geologic heterogeneities on the transport of gas through a saturated system, in which the behaviour of disconnected gas flow and pool height is modified in the presence of unique gas release pathways and conduits. When heterogeneities facilitate the generation of an extended gas pool, stronger buoyant forces are able to easily overcome weakened capillary forces of a contaminated porous medium. However, mobilization of gas in an extended pool will still terminate at a critical height proportional to the reduction in interfacial tension induced.

Based on laboratory flow-cell experiments generated for contamination of a 1-Butanol LNAPL pool on a quasi-saturated groundwater system, an MIP-IFT model was

developed to model the direct effects of concentration-dependent interfacial tension on the initiation, migration and termination of trapped gases in quasi-saturated porous media. The model developed combined a contaminant transport advection-dispersion model with macroscopic invasion percolation to simulate the experiments conducted on the same geologic sand-pack. The model was able to successfully simulate the transport of gas in the presence of aqueous 1-Butanol due to the concentration-dependent reductions in interfacial tension, accurately demonstrating termination of the gas pool to a critical pool height proportional to the reduction in interfacial tension. The model also captured the key mechanisms driving gas flow in a porous medium contaminated with 1-Butanol. Gas migration initiated upon the arrival of the aqueous 1-Butanol front at the upper boundary of the gas pool. Gas flow through a capillary barrier in the model caused a decrease in pool height with time, until terminating at a critical pool height, similar to that observed in laboratory experiments. The mechanisms of the termination of gas flow was the same as that demonstrated in laboratory experiments.

Using the developed model, a sensitivity analysis was performed to investigate the implications of different porous media properties of the capillary barrier and coarse background material on gas migration, in which alterations in material characteristics displayed a direct effect on gas transport mechanisms and termination. The model was determined to be sensitive to pore-scale variabilities of the capillary barrier, in which the fragmentation and migration of gas was influenced by the grain size distribution and hysteretic properties of the material comprising the barrier. Further sensitivity analyses were conducted to simulate the effects of different surfactants of varying strengths on the

mobilization of trapped gases, in which gas flow terminated at a measured pool height proportional to the reductions in interfacial tension induced.

This research provides a further understanding on the mechanisms of gas migration in quasi-saturated porous media, and the implications of chemical surfactants on the mobilization of trapped gases. The fundamental concepts and relationships developed in this work can be further applied to other trapped non-wetting fluids, including NAPL residuals below the subsurface. Biofuel additives function as an alternative to fossil fuels and will continue to be developed and enhanced for use in vehicles and other applications. It is important that future work continues to investigate the potential interactions that take place between modern contaminants and quasisaturated groundwater systems. This work focused on the analysis in an ideal flow-cell configuration to identify the key mechanisms and processes associated with gas migration resulting from contamination with biofuel additives. However, natural deposits would not exhibit the same depositional geometry. This is critical to investigate the effects of biofuel additives when contaminating trapped non-wetting fluids in natural groundwater systems, to understand the implications on hydrogeologic properties in natural porous media. From this work, it is expected that in natural porous media, trapped gases are also influenced by dynamic contact effects. These effects are more pronounced in natural porous media with different surficial wettability properties and may influence the migration and flow of gas in quasi-saturated groundwater systems contaminated with chemical surfactants. Further investigation of the effects of contact angle dynamics on

gas flow will capture a complete representation of non-wetting fluid mobilization contaminated with biofuel additives.

The MIP-IFT model provides a strong foundation for gas transport in contaminated quasi-saturated groundwater systems. This model may be applied to different laboratory-based experiments investigating the effects of different contaminant influences on the migration of non-wetting fluids in a quasi-saturated porous medium. However, this model simulates contaminant transport as one-dimensional advectivedispersive transport and does not capture the influence of geologic heterogeneities on contaminant flow. Further work may modify the MIP-IFT model to enhance the contaminant transport to better fit the flow-regime of the porous medium and improve the reproducibility to experiments conducted in this work. The model was able to capture the mechanisms and behaviours of gas migration exhibited in flow-cell experiments, providing a representation of the physical system. However, the model was limited to uniform porous materials based on the resolution of the grid space applied. Future work to guide hydrogeologic modelers in choosing a model resolution to best represent the physical system will improve the functionality of MIP models in simulating behaviours natural porous media.

Groundwater sources are depleting with overconsumption and contamination, limiting freshwater resources to an ever-increasing human population. As biofuel additives begin to be introduced as a mainstream alternative to fully petroleum-based fuels, understanding the potential implications of the chemicals on natural systems becomes important to limit adverse effects and create necessary remediation technologies.

Appendix

In order to define the statistical population size that captures the average behaviour of immobile gas contaminated with 1-Butanol in the MIP-IFT model, the cumulative average and cumulative variance of the final gas pool height was computed (Figure A.1). In order to ensure the true average was represented, 500 model iterations were conducted.



Figure A.1. Cumulative average and cumulative variance of the final gas pool heights after contamination with 1-BuOH of 500 model realizations.

The result final gas pool heights after contamination with 1-Butanol of 500 model iterations characterized by different pressure distributions exhibited a near proportional decrease in gas pool height to the decrease in interfacial tension (Figure A.2.a-b)

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Figure A.2.a. *Model simulations of the final gas pool height of 500 realizations.* The final results of 500 model iterations, displaying the results of model iteration 1-260.

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Figure A.2.b. *Model simulations of the final gas pool height of 500 realizations.* The final results of 500 model iterations, displaying the results of model iteration 261-500.