INVESTIGATION OF MASS TRANSFER EFFECTS ON NAPHTHA SURROGATES PARTITIONING FROM BITUMEN TO AQUEOUS PHASES IN ATHABASCAN OIL SANDS TAILINGS PONDS

by

Avery Stakenvicius Ling

A thesis submitted to the Department of Chemical Engineering
In conformity with the requirements for
the degree of Master of Applied Science in Chemical Engineering

Queen’s University
Kingston, Ontario, Canada
(September, 2023)

Copyright © Avery Stakenvicius Ling, 2023
Abstract

The Athabasca oil sands deposits are one of the largest in the world. They have been the backbone of the Albertan economy and a major source of energy and petrochemical products in North America for several decades. Approximately half of the region’s bitumen production is generated from open-pit mining and is processed with the Clark’s hot water extraction process (CHWEP). The CHWEP produces and stores significant waste in oil sands tailings ponds (OSTPs). From these OSTPs, there are significant CH₄ and CO₂ emissions from biogenic activity, such as the biodegradation of diluent naphtha. These greenhouse gases (GHGs) are of substantial environmental concern. A better understanding of the mechanisms affecting their emission rates could be used to mitigate these GHG emissions while balancing other environmental concerns within the OSTPs.

Compositional analysis of naphtha is complex, costly and time-consuming. The use of fluorescence spectroscopy with a single wavelength steady-state excitation over a broad emission spectrum range was found to reduce the cost, speed, and complexity of analysis for laboratory experiments to study aqueous soluble naphtha surrogates for bitumen-to-aqueous phase mass transfer experiments.

The bio-accessibility of naphtha to microorganisms limits GHG emission rates. The mass transfer of naphtha surrogates from bituminous to aqueous phases was experimentally found to be severely impacted by the saline concentration of the aqueous phase. A combined theoretical and empirical model indicated that experiments with agitation achieved system equilibrium. The initial concentration of naphtha solubilized within bitumen droplets had minimal impact on mass transfer rates and equilibrium concentrations achieved over sessile 2D diffusional experiments. Sessile diffusional experiments achieved lower apparent equilibria than model predictions or results obtained in agitated (forced equilibria) experiments. Aqueous phase replacement experiments resulted in lower lumped mass transfer rate coefficients and apparent equilibria. These observations indicate that limitations of naphtha transfer to an aqueous phase exist due to low diffusivity rates within the bitumen droplets, developing concentration gradients over time, and/or the formation of an interfacial film between the bituminous and aqueous phases.
Co-Authorships

In this thesis, all the experiments were performed by myself. While I wrote the original draft, I would like to acknowledge the supervision and editing of my thesis by my supervisors, Dr. Juliana Ramsay, Dr. Bruce Ramsay, and Dr. Kevin Mumford, who provided invaluable assistance and guidance. Chapter 3, “Florescence Spectroscopy for Analysis of Aqueous Phase Aromatic Naphtha Surrogates” is being modified to be authored by myself, Bruce A. Ramsay, R. Stephen Brown and Juliana A. Ramsay. Data from Chapter 4 is being used for the preparation of “Effects of Size and Composition of Bitumen Aggregates on Intra-Oil Diffusion and Dissolution of Hydrocarbon Solvents in Froth Treatment Tailings” for publication. This paper incorporates additional modelling by Saeid Shafieiyoun and will be authored by Saeid Shafieiyoun, myself, Bruce A. Ramsay, Juliana A. Ramsay, and Kevin G. Mumford (not yet submitted).
Acknowledgements

I would like to thank all of those who made grad school some of the best years in my life. I am extremely grateful for the opportunity my supervisors, Dr. Juliana and Bruce Ramsay, gave me to work on this project and their continual support, guidance, expertise and patience. I would also like to thank my supervisor, Dr. Kevin G. Mumford and Dr. Saeid Shafieiyoun, for their guidance and for providing the context of further applications to this research. Thank you to Dr. Stephen Brown, Lynne O’Donnell, and Jennie Moe for providing me access and guidance to their lab space, which proved invaluable throughout this project. Especially in the pandemic this would not have been possible during the pandemic had it not been for the hard work and support of our entire lab over the years, especially to Mara Silva, Pedro Manuel, and Hang Li, and I am grateful. There has been much more support and collaboration among Queen’s staff, most notably the Analytical Services Unit staff provided invaluable knowledge and hard work in this project and my growth as a researcher. Thank you to Paula, Mesha, Graham, Dale, and Allison. This work was supported by Imperial Oil Limited and Alberta Innovates through the Institute for Oil Sands Innovation at the University of Alberta (IOSI), as well as Canada's Oil Sands Innovation Alliance (COSIA) with Pathway Alliance, and Natural Sciences and Engineering Research Council of Canada (NSERC). While already mentioned, thank you to my committee of Dr. Nicholas Hudon (Chair), Dr. Juliana Ramsay, Dr. Bruce Ramsay, Dr. Kevin Mumford, Dr. Ehssan Koupae, and Dr. Stephen Brown for all their time and effort.

Outside of academia, I want to thank all my teammates at Queen’s Triathlon who preserved through virtual workouts and numerous restrictions to create a safe environment which helped me maintain my mental health during the pandemic. I want to thank all my friends for their generosity and support, I would not have been able to do this without them. Finally, I want to thank my family. Thank you to my parents Herbert and Kristina, for raising and supporting me in so many ways throughout my entire life. Thank you to my sister Jenna for keeping me grounded and always being there whenever I needed it. To my brother Adrian, thank you for the inspiration to study engineering and for always being supportive and eager to talk about anything with me. To all the above and those who I have not mentioned, I am truly grateful.
# Table of Contents

List of Tables .................................................................................................................. viii  
List of Figures .................................................................................................................. ix  
List of Equations ............................................................................................................ xii  
List of Abbreviations and Symbols ................................................................................. xiii  
Chapter 1 Introduction .................................................................................................... 1   
  1.1 Background ............................................................................................................. 1   
  1.2 Overall Research Objectives ................................................................................... 4   
  1.3 Organization of the Thesis ....................................................................................... 4   
  1.4 References .............................................................................................................. 5   
Chapter 2 Literature Review .......................................................................................... 7   
  2.1 Introduction ............................................................................................................ 8   
    2.1.1 Athabasca Oil Sands Deposits ......................................................................... 8  
    2.1.2 Clark’s Hot Water Extraction Process .......................................................... 8  
    2.1.3 Geochemical Characteristics of Athabasca Oil Sands Tailing Ponds ............ 9  
  2.2 Sources of Environmental Impact ........................................................................... 10  
    2.2.1 Reclamation of Oil Sands Industrially Impacted Land ................................... 10  
    2.2.2 Tailings Waste ................................................................................................. 11  
    2.2.3 Water Pollution ............................................................................................... 12  
    2.2.4 Greenhouse Gas Emissions ............................................................................ 13  
    2.2.4.1 Biogenic Gas Production ......................................................................... 13  
    2.2.4.2 Long Latency Period ................................................................................. 14  
    2.2.4.3 Emissions Measurement ......................................................................... 15  
    2.2.4.4 Biodegradation ......................................................................................... 16  
  2.3 Characterization of Tailing Ponds ......................................................................... 16  
  2.4 Biodegradation Studies ......................................................................................... 17  
    2.4.1 Bitumen Degradation ..................................................................................... 17  
    2.4.2 Labile Component Studies ............................................................................. 17  
    2.4.3 Long-Term Recalcitrant Degradation Studies ............................................... 18  
  2.5 Naphtha Diffusion ................................................................................................. 19  
    2.5.1 Effect on Microbial Activity ......................................................................... 20  
    2.5.2 Mass Transfer Models .................................................................................... 20  
  2.6 Unified Model ........................................................................................................ 24  

\*\*\* \n
v
Chapter 3 Fluorescence Spectroscopy Analysis of Solubilized Aromatic Naphtha Surrogates .......................................................... 33
Abstract .................................................................................................................. 33
3.1 Introduction ......................................................................................................... 34
3.2 Materials and Methods ....................................................................................... 38
   3.2.1 Fluorescence Spectroscopy Methodology ...................................................... 38
   3.2.2 Selection of Naphtha Surrogates ................................................................. 39
   3.2.3 Effect of Methanol (as a co-solvent) on minimizing loss of surrogates ........ 39
   3.2.4 Interference between surrogates (o-xylene and 1-MN) ............................... 40
   3.2.5 Interference between naphtha surrogates and bituminous components .... 40
   3.2.6 Effect of solution salinity on fluorescence .................................................. 41
   3.2.7 Analysis of surrogates in MFT .................................................................... 41
   3.2.8 Statistical analysis of surrogates ................................................................. 41
3.3 Results and Discussion ....................................................................................... 42
   3.3.1 Selection of Naphtha Surrogates ................................................................. 42
   3.3.2 Selection of a Co-Solvent ............................................................................ 42
   3.3.3 Effect of MeOH Concentration and Sample Storage Time ....................... 43
   3.3.4 Interference between Naphtha Surrogates .................................................. 44
   3.3.5 Interference between Surrogates and Bitumen .......................................... 45
   3.3.6 Effect of Contact Time of Bitumen with Aqueous Phase ......................... 47
   3.3.7 Effect of Salinity on Fluorescence .............................................................. 50
   3.3.8 Analysis of Surrogates in MFT .................................................................. 52
3.4 Conclusions ....................................................................................................... 55
3.5 References ......................................................................................................... 57
Chapter 4 Mass Transfer of Naphtha Between Bitumen and Aqueous Phase .......... 60
Abstract .................................................................................................................. 60
4.1 Introduction ....................................................................................................... 61
4.2 Material and Methods ....................................................................................... 63
   4.2.1 Separation of Bitumen from Bitumen Froth ................................................. 63
   4.2.2 Bitumen Characterization ........................................................................... 63
   4.2.3 Spiking Bitumen with Naphtha Surrogates ............................................... 64
   4.2.4 Simulated Oil Sands Tailings Pond Pore Water ......................................... 64
   4.2.5 Mass Transfer Experiments ...................................................................... 64
List of Tables

Table 2.1: Pertinent characteristics of oil sands tailing ponds ................................................................. 14

Table 2.2: Hydrocarbons studied and modelled regarding the degradation kinetics over long periods. .... 19

Table 3.1: Total organic carbon (%) of MFT solids after five extractions with RO water or 20% MeOH. 54

Table 4.1: A table summarizing the four conditions tested independently in the diffusional mass transfer experiments. ............................................................................................................. 66

Table 4.2: Summary of the lumped mass transfer parameters fit for the post-replacement data in Figure A4.4........................................................................................................................................ 81

Table 4.3: Summary of biodegradation rates of naphtha and/or naphtha surrogates normalized to 23 mL working volume, with their inoculum source and journal article. ............................................... 82

Table 4.4: Summary of mass transfer rates of naphtha surrogates normalized to a 23 mL working volume. ........................................................................................................................................ 83

Table A4.1: Weight retained for 1 g each of toluene, o-xylene, nonane and 1-MN after heating at different temperatures for 30 min and 5 min of mixing. ........................................................... 113

Table A4.2: Viscosities of bitumen spiked with 0, 1, 2, or 4 wt.% o-xylene and 1-MN and of bitumen alone ........................................................................................................................................ 113

Table A4.3: Summary of f-test and t-test results for evaluating differences in apparent equilibrium values for sessile droplet diffusional and forced equilibrium experiments using RO water. ...................... 115

Table A4.4: Summary of f-test and t-test results for evaluating the difference in apparent equilibrium values for sessile droplet diffusional and forced equilibrium experiments using simulated tailing pond pore water. ........................................................................................................ 116

Table A4.5: Summary of F-test and T-test results in evaluating differences in apparent equilibria for sessile droplet diffusional replacement of the aqueous phase ° experiments and forced equilibria experiments using simulated OSTP pore water. ................................................................. 116

Table A4.6: Summary of the lumped mass transfer parameters used in Equation 4.2 And represented in Figure 4.6. ........................................................................................................................................... 119

Table A4.7: Summary of F-test and T-test results for evaluating the difference in apparent equilibria values for sessile droplet diffusional replacement of aqueous phase experiments and forced equilibria experiments using RO water. ........................................................................................................ 119

Table A4.8: The variables used in the combined empirical and fugacity-based equilibrium model, and their respective symbols and units. .................................................................................................. 122
List of Figures

Figure 1.1: Theoretical cross-section of the tailings pond. Bitumen sinks through the process affected (PA) water, fine fluid tailings (FFT), mature fluid tailings (MFT), and sand. Volatilization of various hydrocarbons exists at (A, B, and C) and decreases at (D) (Small et al. 2015). ................................. 2

Figure 2.1: Schematic of an emission isolation flux chamber measuring gas emission rates from surfaces . ........................................................................................................... 15

Figure 2.2: Schematic of the release of organic hydrocarbons from a NAPL phase. ........................................... 21

Figure 2.3: Schematic of the physical system simulated consisting of a spherical NAPL blob suspended in a volume of water.......................................................... 22

Figure 3.1: Fluorescence of naphtha surrogates as a function of time after equilibration with bitumen for 1 d, samples were analyzed after 0, 6, and 19 days. ................................................................. 44

Figure 3.2: Fluorescence emission spectra of 1 mg/L o-xylene with 1-MN varying from 10 µg/L to 10 mg/L to test for the interference of fluorescence response when excited at 260nm. .......................... 45

Figure 3.3: The fluorescence emission spectra of preparations excited at 260 nm for (a) naphtha diluted in RO water, RO water in contact with a bitumen droplet, and RO water in contact with a bitumen droplet and spiked with naphtha and, (b) naphtha diluted in RO water, RO water sample in contact with a bitumen droplet, and RO water sample in contact with a bitumen droplet spiked with naphtha. ............................... 47

Figure 3.4: Fluorescence emission spectra for aqueous samples from 1, 4, and 9 d of contact with a bitumen droplet. ........................................................................................................ 48

Figure 3.5: Fluorescence of naphtha surrogates as a function of time after equilibration with bitumen for 1 and 9 d........................................................................................................ 49

Figure 3.6: Calibration curves of (a) o-xylene and (b) 1-MN in 3 solutions: RO water, RO water with 20% HPLC grade MeOH, and a simulated OSTP pore water with 20 vol.% HPLC grade MeOH .......................... 51

Figure 3.7: 1-ring aromatic concentration as a function of the number of extractions with fresh RO water or 20% MeOH in RO water of MFT samples with and without spikes of o-xylene ........................................ 53

Figure 4.1: (Left) photo of centrifuge tubes containing bitumen froth after centrifugation with reverse osmosis water. (Right), a cross-sectional schematic illustrating the relative amount of solids, bitumen, aqueous and light non-aqueous (LNAPL) phases. .......................................................... 63

Figure 4.2: Schematic of the experimental setups where (Left) is the sessile diffusional experiment. (Right) depicts an agitation-forced equilibrium experiment. .......................................................... 65

Figure 4.3: Forced equilibrium concentrations of o-xylene and 1-MN partitioning from bitumen into RO or simulated OSTP pore water as a function of their initial mole fraction within the bitumen droplet. .......... 68

Figure 4.4: Aqueous phase concentrations as a function of the initial mole fraction of naphtha surrogate in the bituminous phase compared with theoretical fugacity-based model predictions. ........................................ 70
Figure 4.5: Aqueous concentrations of naphtha surrogates in sessile bitumen droplet diffusion experiments in simulated OSTP pore water. ................................................................................................................. 72

Figure 4.6: Integrated mass transfer data for the sessile bitumen droplet experiments (Equation 4.2), of (a) 4 wt.% o-xylene in RO water and (b) 4 wt.% 1-MN in simulated OSTP pore water. ......................................................... 75

Figure 4.7: Aqueous concentrations of the sessile diffusional experiments (pre-replacement) are overlayed with the concentrations of the aqueous phase replacement experiments (post-replacement) for comparison. ........................................................................................................................................ 78

Figure 4.8: Integrated mass transfer data for the post-replacement sessile bitumen droplet experiments of (a) 2 wt.% o-xylene in RO water and (b) 4 wt.% 1-MN in OSTP pore water. ................................................................. 80

Figure A3.1: 1-MN calibration curves for the integrated ranges of 315-410nm (in RO water). ........... 104

Figure A3.2: The fluorescence emission spectra for toluene (d), o-xylene (b), and 1-MN (c) are shown when excited at 260 nm in an aqueous solution. An anthracene standard ((a) used for device calibration) fluorescence emission spectra is shown (top right) when excited at 310 nm. ......................................................... 105

Figure A3.3: Integrated areas from fluorescence analysis of o-xylene and 1-MN in 20% MeOH and RO water at ~ 5 min intervals................................................................................................................................. 106

Figure A3.4: Fluorescence spectroscopy responses of microcosms enriched with naphtha, toluene and 1-MN or o-xylene and 1-MN. ..................................................................................................................... 106

Figure A3.5: Integrated fluorescence responses of o-xylene at different ratios with 1-MN (left) and 1-MN when at different ratios with o-xylene. ........................................................................................................ 107

Figure A3.6: Calibration curves of o-xylene and 1-MN in solutions with “background” bitumen signal solutions in 20% MeOH in RO water to ensure the linearity of a fluorescence response still occurs in the presence of other bituminous molecules when excited at 260 nm. ...................................................................................... 108

Figure A3.7: Fluorescence emission spectra of serial dilution of o-xylene and 1-MN in simulated OSTP pore water with 20 vol.% HPLC grade MeOH. (a) shows 4 dilutions of o-xylene and 1-MN at a 10:1 ratio (o-xylene concentration stated. First, 1-MN stated second) along with a blank solution with no o-xylene or 1-MN. (b) contains no new information but is zoomed in at the lowest two concentrations, and the solvent blank with a different y-axis to visualize the data better. ........................................................................................................ 109

Figure A3.8: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment only using 20% MeOH on Pond B - 12.5 m samples. ................................................................. 109

Figure A3.9: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment only using 20% MeOH on Pond A - 5 m samples. ................................................................. 110

Figure A3.10: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment on Pond B - 12.5 m samples. ........................................................................................................ 110

Figure A3.11: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment on Pond A - 5 m samples. ........................................................................................................ 111
Figure A3.12: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment on Pond A - 5 m samples. .........................................................................................................................111

Figure A3.13: Calibration curves for (a) o-xylene and (b) 1-MN in the simulated OSTP pore water with both the linear ranges that were used for the calibration curves and non-linear ranges which were omitted for the calibration curves. .................................................................................................................................112

Figure A4.1: Residual plots from the linear regression of the forced equilibrium experiments (Figure 4.5) for o-xylene (a) and 1-MN (b) in simulated OSTP pore water. .................................................................................................................................114

Figure A4.2: Integrated mass transfer data for the sessile bitumen droplet experiments, of 2% o-xylene and 1-MN in RO water (a and b), 4% o-xylene and 1-MN in RO water (c and d), and o-xylene and 1-MN in simulated tailing pond pore water (e and f). .................................................................................................................................117

Figure A4.3: Plots of the residuals between the fitted lambda lumped mass transfer rate models and the experimental aqueous concentrations from the sessile diffusional experiments. .................................................................................................................................118

Figure A4.4: Integrated mass transfer data for the post-replacement sessile bitumen droplet experiments of 2% o-xylene and 1-MN in RO water (a and b), and 4% o-xylene and 1-MN in simulated tailing pond pore water (c and d). ........................................................................................................................................120

Figure A4.5: Plots of the residuals between the fitted lambda lumped mass transfer rate models and the experimental aqueous concentrations from aqueous phase replacement experiments. ......................................................121
List of Equations

Equation (2.1): \[ \frac{\partial C_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \sum_{j=1}^{n-1} D_{ij} \frac{\partial C_j}{\partial r} \right) \] .......................................................... 23

Equation (2.2): \[ \frac{\partial C_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \sum_{j=1}^{n-1} D_{ij} \frac{\partial C_j}{\partial r} \right) \] .......................................................... 23

Equation (2.3): \[ \frac{\partial C_i^w}{\partial t} = \lambda_i (C_{eq,i}^w - C_i^w) - k_i C_i^w \] .......................................................... 24

Equation (4.1): \[ \frac{\partial C_i^w}{\partial t} = \lambda_i (C_{eq,i}^w - C_i^w) - k_i C_i^w \] .......................................................... 74

Equation (4.2): \[ 1 = \frac{c_i^w}{c_{eq}} = p * e^{\lambda_i t} \] .......................................................... 75

Equation A4.1: \[ C_x = Z_x V_x \] .......................................................... 123
### List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BML</td>
<td>Base Mine Lake</td>
</tr>
<tr>
<td>BTEX</td>
<td>Benzene, toluene, ethylbenzene, and xylenes</td>
</tr>
<tr>
<td>CAT</td>
<td>Computed Axial Tomography</td>
</tr>
<tr>
<td>CHWEP</td>
<td>Clark’s Hot Water Extraction Process</td>
</tr>
<tr>
<td>CWD</td>
<td>Course Wood Debris</td>
</tr>
<tr>
<td>DEHP</td>
<td>di(2-ethylhexyl)phthalate</td>
</tr>
<tr>
<td>DNAPL</td>
<td>Dense Non-aqueous Phase Liquid</td>
</tr>
<tr>
<td>EPL</td>
<td>End Pit Lake</td>
</tr>
<tr>
<td>ERCB</td>
<td>Energy Resources Conservation Board</td>
</tr>
<tr>
<td>FFT</td>
<td>Fluid Fine Tailings</td>
</tr>
<tr>
<td>FID</td>
<td>Flame Ionization Detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse Gas</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>LNAFL</td>
<td>Light Non-aqueous Phase Liquid</td>
</tr>
<tr>
<td>MEK</td>
<td>Methyl-ethyl Ketone</td>
</tr>
<tr>
<td>MFT</td>
<td>Mature Fine Tailings</td>
</tr>
<tr>
<td>MLSB</td>
<td>Mildred Lake Settling Basin</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>NAPL</td>
<td>Non-aqueous Phase Liquid</td>
</tr>
<tr>
<td>OSTP</td>
<td>Oil Sands Tailings Pond</td>
</tr>
<tr>
<td>PA</td>
<td>Process Affected</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>RET</td>
<td>Resonance Energy Transfer</td>
</tr>
<tr>
<td>SPME</td>
<td>Solid Phase Microextraction</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermoconductivity Detector</td>
</tr>
<tr>
<td>TMF</td>
<td>Tailings Management Framework</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Lumped Mass Transfer Rate Coefficient</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Background

The Athabascan oil sands deposits are mixtures of silt, quartz sand, clay, bitumen, pore water and trapped gases that cover 142,200 km$^2$ (Lo et al. 2006; Small et al. 2015). When open pit mining, the Clark’s hot water extraction process (CHWEP) for bitumen involves additives such as caustic soda, sodium nitrate and a naphtha based or paraffinic diluent. These additives help separate bitumen from undesired material such as dissolved metals, clay, water, and other solids. These waste products are sent into the oil sands tailings ponds (OSTPs) for storage. Due to inefficiencies in the CHWEP and naphtha recycling, naphtha solubilized in bitumen is also sent into these ponds for storage (Chalaturnyk et al. 2002; Siddique et al. 2012). Due to decades of industry, these ponds cover ~220 km$^2$ in the Athabascan region (Small et al. 2015).

Over time these ponds develop layers. The top 2-10 m from the surface is oil sands process affected (PA) water, while deeper layers are Fluid Fine Tailings (FFT) and then Mature Fluid Tailings (MFT) (up to 40 m depth) (Foght et al. 2017). Bitumen can be found in all layers of these ponds, increasing density and anaerobic conditions with respect to depth in the OSTPs (e.g., less dense slicks remain at or near the surface) (see Figure 1.1) (Dompierre et al. 2016).
Figure 1.1: Theoretical cross-section through the centre of a tailings pond. This is a pond that is currently in operation for decades. Bitumen sinks through the process affected (PA) water, fine fluid tailings (FFT), mature fluid tailings (MFT), and sand. GHG emissions from (A) light volatile organic compounds volatilizing at the surface, the aerobic (B) and anaerobic (C, D, and E) degradation of various hydrocarbons at various depths, where (E) indicates GHG trapped in the pore spaces of the MFT. Adapted from (Small et al. 2015).

After decades, significant greenhouse gas (GHG) emissions emerge from those ponds (e.g., ~15 years for the first observed emissions for Syncrude’s Mildred Lake Settling Basin and is about 11,200 tons of CH₄ per year after 36 years) (Small et al. 2015). Overall, an estimated 33,100 tons of CH₄ and 423,000 tons of CO₂ are emitted every year from Suncor’s, Syncrude’s, and Shell Albian’s ponds in the Athabasca region which accounts for 0.65% of the industries GHG emissions (Baray et al. 2018; Foght et al. 2017; Oil Sands Discovery Center (OSDC), 2023). While 0.65% is not a large portion of the emissions, it is not negligible. Hence, this work is focused on the MFT several meters deep in OSTPs that are producing GHG emissions (after several decades of use). Beyond the initial lag phase, GHG emission rates can be impacted by the following:
• GHG diffusivity through the MFT/FFT/PA water
• Biodegradation rate of the substrate contributing to the GHGs (e.g., naphtha)
• Bioavailability of naphtha (e.g., mass transfer from the bituminous to aqueous phase)
• Bioavailability of necessary nutrients for growth (e.g., a nitrogen or phosphorus source)

Of all the GHGs emitted from the OSTPs, CH₄ is of the greatest concern as it has a global warming potential 27-30 times greater than CO₂ over 100 years as of July 31st 2023 (US EPA 2023), and it is produced from the biodegradation of naphtha via two primary processes (Baray et al. 2018; Foght et al. 2017; Kong et al. 2019). First, free hydrocarbons (e.g., bioavailable naphtha) are degraded into complex metabolites (e.g., naphthenic acids or alcohols), which are, in turn, further degraded to simpler metabolites (e.g., formate and acetate) and then to GHGs (e.g., CH₄ and CO₂). These biodegradation pathways are often performed by mixed microbial populations and produce a variety of metabolites via complex mechanisms.

Naphtha biodegradation in the MFT of OSTPs has been well studied (Siddique et al. 2006, 2007, 2008). However, it has been shown that there are limitations to biodegradation rates, of which naphtha bioavailability is a possible cause (Ramsay et al. 2021). Furthermore, naphtha bioavailability can be affected by its mass transfer from bituminous to aqueous phases, on which there is limited research. However, there have been investigations on similar topics, such as empirical studies of the mass transfer of light hydrocarbons from coal tar (derived from former manufacturing gas plants) into aqueous phases. The resulting data were fitted to a multicomponent-multiphase model (Shafieiyoun & Thomson, 2018).

Naphtha is comprised of many different C5-10 hydrocarbon constituents that can make accurate and specific compositional analysis both expensive (up to $200 per sample) and difficult (Moe 2021; Speight, 2019). These hydrocarbon constituents are ~7% cyclohexanes, ~15% cyclopentanes, ~31% larger compounds of unconfirmed composition such as naphthalenes, and the majority of the remainder being primarily linear alkanes (Speight, 2019).

Beyond technical and environmental concerns, the government of Alberta implemented a Tailings Management Framework (TMF), including various rules and constraints around the production and, most
notably, management of tailings which provides further motivation to research this topic (Dompierre et al. 2016; Government of Alberta, 2015).

1.2 Overall Research Objectives

The goal of this research is to develop a better understanding of how bituminous and aqueous phase compositions affect the presence of naphtha in the aqueous phase of MFT in the Athabasca OSTPs. This will be accomplished by performing empirical mass transfer studies of naphtha surrogates from bituminous to aqueous phases in a variety of conditions. The results of these experiments will be used to supplement and develop models to investigate the variety of conditions found in Athabascan OSTPs. The specific research objectives of this work are:

1. Develop an analytical method to accurately, reliably, and quickly determine the aqueous phase concentration of naphtha surrogates in the presence of bitumen and salts in an affordable manner such that it is feasible to perform many experiments.

2. Investigate how the naphtha concentrations in bitumen, and aqueous phase saline concentrations and their interfaces experimentally affect the rates of naphtha mass transfer from the bituminous into the aqueous phases.

3. Use experimental data to develop models that describe and predict the mass transfer phenomena between bituminous and aqueous phases.

Information derived from these research objectives will help guide the direction of future research as well as the applications of current technologies dealing with OSTP reclamation and the GHGs emitted from them as the mass transfer limitations of naphtha must be considered in biodegradation studies.

1.3 Organization of the Thesis

This thesis is presented in a manuscript format, where the methodology and results chapters (Chapters 3 and 4) are formatted for publication in peer-reviewed journals. Chapter 2 provides a literature review of the industrial practices in the Athabasca Oil Sands, the nature of OSTPs in that region, concerns and
challenges regarding the OSTPs, GHG emissions from them and OSTP reclamations, and the current state of research on these subjects. Chapter 3 tackles research objective (1) by developing an analytical fluorescence spectroscopy method to measure the aqueous phase concentration of 1-ring and 2-ring aromatic compounds. Chapter 4 deals with research objectives (2) and (3) with the methodology, results, and analysis of sacrificial mass transfer experiments of naphtha surrogates from the bituminous and aqueous phases. The overall conclusions and recommendations for future work are shown in Chapter 5.

The appendix includes supplemental fluorescence spectroscopy results, information used in a fugacity-based validation model, OSTP pore water analytical results, and GC-TCD calibration curves. Due to the manuscript format, some information will overlap between Chapter 1, Chapter 2 and the introduction of Chapters 3 and 4.

1.4 References


Chapter 2

Literature Review

Abstract

The oil sands deposits in the Athabasca region of northern Alberta are one of the largest oil deposits in the world. Being a backbone of the Albertan economy and a source of energy and petrochemical products in North America, the infrastructure/industry surrounding these deposits is significant. The hot-water process for extracting bitumen from sands, silts, clays, and other impurities in the oil sands deposits varies among operators yet often involves diluent solvents. Diluent naphtha is a commonly used mixture of benzenes, toluenes, ethylbenzenes, and xylenes (BTEXs), aliphatic, and polycyclic-aromatic hydrocarbons. While the majority of this naphtha is recovered and recycled in the process, a small portion of this naphtha is sent to tailing ponds solubilized in bitumen along with sands, silts, clays and water. The solids gradually settle to the bottom of these ponds over a period of years. Significant CH\textsubscript{4} and CO\textsubscript{2} emissions are observed at the surfaces of these tailing ponds. These gases are generated from the biodegradation of naphtha components and other hydrocarbons. This complex system is not well understood. Research on the main effects of this is summarized, including but not limited to other environmental concerns from the oil sands industry, policies, variability among ponds, mass transfer limitations, nutrient availability, lag times, and the variability in natural systems. The progress in this field is promising and future work could lead to the ability to investigate potential treatment methods for oil sands tailings ponds.


2.1 Introduction

2.1.1 Athabascan Oil Sands Deposits

The major oil sands deposits of Athabasca, Cold Lake and Peace River account for ~39% of Canada’s total oil production and contain an estimated 1.7-2.5 trillion barrels of bitumen (Small et al. 2015). Specifically, the Athabascan oil sands are one of the world's largest petroleum reserves, covering 142,200 km² (Oil Sands Discovery Center (OSDC), 2023; Small et al. 2015). The Canadian oil sands are a mixture of silt, quartz sand, clay, bitumen, pore water and trapped gases, where bitumen is the desired product (Lo et al. 2006). In addition, approximately half of the bitumen production in the region was generated from open-pit mining and is generally processed by the Clark’s hot water extraction process (CHWEP) (Alberta Energy Regulators (AER), 2023).

2.1.2 Clark’s Hot Water Extraction Process

In surface mining, the ore is processed by the Clark hot water extraction process (CHEWP), where bitumen is separated from undesired oil sands constituents (Clark & Pasternack, 1932). Mined oil sands ores are mixed with hot water/steam and caustic soda, where the oil sands separate, leaving the densest constituents such as silts, sands, and clays at the bottom (removed as whole tailings waste) while the water and bitumen are in the middle/top due to their similar densities (Clark & Pasternack, 1932). The water/bitumen stream is then de-aerated and mixed with a hydrocarbon diluent (e.g., a naphtha or paraffinic solvent) to enhance recovery and decrease bitumen viscosity for better flow through pipelines (Clark & Pasternack, 1932). After another separation stage, the bitumen is skimmed off the top of the surface as a bitumen froth and sent for upgrading. Some diluent is recovered and recycled at this stage, resulting in another waste stream of primary water. As one volume of oil sands ore requires three volumes of water to process, the CHWEP generates large volumes of waste called froth treatment tailings (FTT) (Holowenko et al. 2002). All this waste must be stored in oil sands tailings ponds (OSTPs) as it cannot be released into the environment because of its toxicity (Foght et al. 2017). FTT contains ore solids (~17%), process water, ~5% unextracted bitumen and
up to 2% unrecovered diluent (Rao & Liu, 2013). Various additives used in the CHWEP can also exist in the FTT (often solubilized in process water), such as caustic soda, sodium citrate and lime/gypsum (Chalaturnyk et al. 2002; Siddique et al. 2012; Small et al. 2015).

2.1.3 Geochemical Characteristics of Athabascan Oil Sands Tailing Ponds

The froth treatment tailing stream eventually ends up in large tailing ponds. Oil sands process affected (PA) water often occupies the top 2-10 m of oil sands tailings ponds, while settled-out solids will occupy the rest of the pond depth (>40 m deep until the mudline in mature tailing ponds) (Foght et al. 2017). These tailing ponds cover a large surface area. For example, Base Mine Lake has a surface area of 8 km² (Dompierre et al. 2016). Bitumen is often found in the pond's PA water or the fluid Fine Tailings (FFT) section. Bitumen slicks often accumulate at the surface yet can also be found deeper in the pond, with small volumes even reaching the Mature Fluid Tailings (MFT) section of the pond (see Figure 1.1) (Dompierre et al. 2016).

Bitumen is a mixture of PAHs and other hydrocarbons. Bitumen has toxic components, and when combined with the other waste products in the oil sands tailings, it contributes to changes with respect to depth in the ponds (such as increasing anoxic conditions and decreasing pH) (Dompierre et al. 2016). The components of bitumen that solubilize in the PA water also result in large volumes of water that are unusable for purposes besides the oil sands industry. The storage of the tailings waste (both solids and liquid) also results in large areas of land that are not usable for any other purpose. Consequently, the ponds pose significant health risks to the environment and surrounding wildlife; these conditions will not change unless action is taken (Mukherji et al. 1997).

Furthermore, the ponds' deeper layers with higher solids content (e.g., MFT) still exist as a watered slurry. If the upper layers of the ponds were removed (e.g., FFT and PA water), this would not be suitable for ground stability. The Alberta government introduced a Tailings Management Framework (TMF) to guide and manage FFT in the Athabasca Oil Sands Region (Dompierre et al. 2016). It includes various constraints and rules; most notably, the TMF mandates that “the entire FFT production from a project must
reach an acceptable state within 10 years of the end of bitumen mining”. This acceptable state is a function of many parameters and is changing over time as more knowledge is acquired (Government of Alberta, 2015). Hence companies are concerned with the fate of their tailings waste.

2.2 Sources of Environmental Impact

2.2.1 Reclamation of Oil Sands Industrially Impacted Land

Land reclamation is returning disturbed land to reuse or to its original ecosystem (NRCA, 2020b). Specifically, the Athabasca oil sands are located in a Boreal Forest that is one of the largest in the world and can sequester about twice the carbon of other forests for thousands of years (NRCA, 2020a). Reclamation of the affected land (662 km² by 2011 but consistently increasing) to the original boreal ecosystem would not only minimize the negative impact of land usage but help sequester carbon (Daly, 2011; NRCA, 2020a).

There are several steps involved in reclaiming land.

1. Re-contouring the ground and installing drainage systems to mimic the drainage of the original landscape.
2. Replacing the top and subsoil layers and organic material similar to the original land.
3. Revegetating the land and seeding with native plants.
4. Monitoring the quality of the soil, ground and surface water, and vegetation over the course of the vegetation growth.

A common tree in the boreal forest, the trembling aspen, is used in ground contouring, drainage and shade removal, and soil treatment crucial for full ecosystem recovery (Naeth et al. 2013; Pinno et al. 2012). Oil sands mines can be active for up to 50 years before decommissioning and can take more than 15 years for certified reclamation (Audet et al. 2015; CAPP, 2020). The industrial best practice is “progressive reclamation,” which begins the reclamation process where possible while the land is still being used.
Depending on how the land is used, some processes can be started, such as the growing and planting of aspen seedlings, which speeds up the long overall reclamation process (Naeth et al. 2013; Pinno et al. 2012).

Biogeochemistry of the soil plays a huge role in the long-term health of the boreal forest ecosystem, as it impacts nutrient cycling and soil microbial composition (Audet et al. 2015). Furthermore, industrial use of river water and groundwater can impact the land hydrology and consequently affect the health of the local ecosystems. Currently, only ~11% of the active mining footprint has been reclaimed or is being reclaimed (CAPP, 2020).

2.2.2 Tailings Waste

While fugitive emissions from these tailing ponds are the focus of this research, other environmental impacts should be acknowledged. Most notable are the toxic effects of the solid tailings impacting the aqueous phase making reclamation extremely difficult (Dompierre et al. 2016). The ERCBs’ TMF has a ten year timeline for the reclamation of FFT providing legal motivations to accelerate tailings reclamation (ERCB, 2013).

Dry sediments must support the weight of vehicles and hence need chemical or physical manipulation of MFT to increase the solids content and recover the removed water where possible. These de-watered tailings can be placed in used-up mining pits and covered with sand, soil, and vegetation. Alternatively, semi-solid tailings in a basin can be covered with fresh water to create an “end lake pit” (EPL) wetland.

De-watered tailings can be obtained by atmospheric drying, spreading fluid tailings thinly with polymers and flocculants, resulting in dry clay (Alberta Environment and Parks, 2020; ERCB, 2013). Most successfully (with Syncrude and Suncor), tailings can be centrifuged to be de-watered into a paste, which is spread thinly, covered with coke, and then revegetated for land reclamation (Alberta Environment and Parks, 2020; Energy Inc, 2022; Kasperski & Mikula, 2011). Cheaper methods involving cyclones and/or other thickeners/coagulants (e.g., gypsum) to create thick, stable slurries have met limited success (ERCB, 2013). Fines can be alternatingly layered with coarse sand and slowly drained over time on pilot scales.
(Kasperski & Mikula, 2011). However, these methods require significant oversight as predicting the volume and quality of tailings produced is difficult due to the natural variability of oil sands deposits. The implications of incorrect predictions are high, with some mines producing up to 1 million tonnes of material daily (Wells, 2011).

To achieve a “wet pond” or “pit lake,” MFT can be pumped from existing tailing ponds into a mined pit area and covered with a layer of water intended to trap the MFT from exposure to the environment (Nix & Martin, 1992). The water would become toxic with diluents, yet it is shown that some stimulation can cause aerobic degradation of the diluents to sufficient environmental levels (Foght et al. 2017; Nix & Martin, 1992). However, best practices indicate that pre-treatment of tailings before disposal in a pit lake may be optimal (Nix & Martin, 1992).

### 2.2.3 Water Pollution

The oil sands industry significantly impacts the quality and availability of water in the Athabasca region, most notably the Athabasca River. While there are limits on the volume of water that can be extracted from the river, there are concerns about the long-term effects. The water stored in the OSTPs is mostly contaminated from the CHEWP, resulting in an alkaline, acutely toxic brackish water with a high concentration of organics. Some of these pollutants have also reached the Athabasca River (Schindler, 2014). While water treatment is often coupled with tailings waste, there has been much ex-situ treatment of water that covers tailings and is used to reclaim local wetlands.

Extensive research indicates that acutely toxic organics in water take several months to two years to degrade (Daly, 2011). However, in end pit lakes, substantial greenhouse gas (GHG) emissions are produced from the MFT. A potential solution is water reclamation through wetland projects. Oil sands PA water can be treated with dug lands seeded with plants and microbes. While promising, these wetlands are on small scales and have minimal or treated (consolidated or non-segregating) tailings. Larger-scale end pit lakes have MFT layered at the bottom and are covered with PA water (Daly, 2011).
Due to a zero-discharge policy, there has been a reduction in water drawn from the Athabasca River and, consequently, more recycled tailings pond water into the CHWEP (Allen, 2008). However, decreasing water quality leads to more issues in eventual water treatment reduction in process efficiency, resulting in more waste bitumen and diluent, worsening environmental issues of toxicity and GHG production (Allen, 2008). In addition, bitumen/oil slicks observed on the surfaces of these tailing ponds harm waterfowl as they can land on the water, get oiled, and drown (CAPP, 2022). A water treatment system could deal with bitumen slicks to increase recycled water quality. A pilot-plant system was implemented to treat oil sands PA water: the raw contaminated water is run through a bio-filter, followed by an ozonation reactor, then another biofilter removing approximately 90% of the naphthenic acids and 34% of oxidized naphthenic acids in the oil sands affected water (Zhang et al. 2019). The unique combination of these three units in succession is more successful than other combinations, while the relatively large scale (200 L) suggests the feasibility of scaling this to be implemented in the industry (Zhang et al. 2019).

2.2.4 Greenhouse Gas Emissions

2.2.4.1 Biogenic Gas Production

Figure 1.1 shows the four main sources of GHG emissions from the OSTPs: (A) Light volatile organic compounds (VOCs) volatilize due to splashing on the pond’s surface, solar heating, and strong winds; (B) Oil slicks at or near the surface can be partially bio-degraded aerobically emitting gases such as CO₂ or light VOCs; (C-D) The anaerobic degradation of organics (primarily naphtha or paraffinic diluents) deeper in the ponds generates CH₄; (E) Large volumes of gases can be trapped in pockets at the lower levels of the MFT. Trapped gases are estimated to be 2-5% of the Mildred Lake Settling Basin (MLSB) overall volume (Holowenko et al. 2000).

The microbial populations within MFT produce GHG emissions such as CO₂, CH₄, and H₂S (Foght et al. 2017). The organic compounds of diluents (naphtha) and lighter bitumen compounds are known to be degraded as a part of this GHG production (Small et al. 2015). These degraders are hypothesized to exist in the aqueous phase near the non-aqueous phase liquid (NAPL) or at the aqueous/NAPL interface (Foght
et al. 2017). Hence, the mass transfer rate of bitumen/naphtha components from the NAPL to the aqueous phase is of interest in the degradation of bitumen/naphtha.

### 2.2.4.2 Long Latency Period

Gas bubbles were noticed at the surfaces of OSTPs such as Mildred Lake Settling Basin and West In-Pit (WIP) within 15 years and 1-2 years of initiating tailing deposits, respectively. However, the Aurora Settling Basin has not had any methanogenic activity in 15 years of operation (Foght et al. 2017). The wide range of tailing ponds in age, diluent and processing (Table 2.1) can lead to various GHG emissions. Laboratory microbial cultures grown on a portion of naphtha constituents have reported yields of 280 m$^3$ of CH$_4$ (~0.2 tonnes) generated per tonne of naphtha (Siddique et al. 2012).

**Table 2.1: Pertinent characteristics of oil sands tailing ponds.**

<table>
<thead>
<tr>
<th>Operator</th>
<th>OSTP Name</th>
<th>Age (years)</th>
<th>Diluent</th>
<th>Process Summary</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suncor</td>
<td>Pond 1A</td>
<td>~55</td>
<td>Light naphtha</td>
<td>Hot water ($\geq$50 °C), NaOH</td>
<td>(Foght et al. 2017)</td>
</tr>
<tr>
<td></td>
<td>Pond 5 and Pond 6</td>
<td>~15</td>
<td>Light naphtha</td>
<td>Hot water ($\geq$50 °C), NaOH, gypsum, sand (CT process)</td>
<td>(Foght et al. 2017)</td>
</tr>
<tr>
<td></td>
<td>Fort Hills</td>
<td>~6</td>
<td>Paraffinic</td>
<td>High temperature (70-90 °C) paraffinic treatment</td>
<td>(Oil Sands Magazine, 2021)</td>
</tr>
<tr>
<td>Shell Canada</td>
<td>Muskeg River</td>
<td>~21</td>
<td>Paraffinic</td>
<td>Trisodium citrate, polymer, low temperature paraffinic treatment (30-50 °C)</td>
<td>(Foght et al. 2017; Oil Sands Magazine, 2021)</td>
</tr>
<tr>
<td></td>
<td>Jackpine</td>
<td>~13</td>
<td>Paraffinic</td>
<td>High temperature (70-90 °C) paraffinic treatment</td>
<td>(Oil Sands Magazine, 2021)</td>
</tr>
<tr>
<td>Syncrude</td>
<td>Mildred Lake Settling Basin</td>
<td>~45</td>
<td>Heavy naphtha</td>
<td>Hot water ($\geq$50 °C), NaOH</td>
<td>(Foght et al. 2017)</td>
</tr>
<tr>
<td></td>
<td>West-In-Pit</td>
<td>~25</td>
<td>Heavy naphtha</td>
<td>No additional chemicals</td>
<td>(Foght et al. 2017)</td>
</tr>
<tr>
<td></td>
<td>Aurora Settling Basin</td>
<td>~20</td>
<td>None</td>
<td>Warm water (35-40 °C), NaOH</td>
<td>(Foght et al. 2017)</td>
</tr>
<tr>
<td>CNRL</td>
<td>Horizon</td>
<td>~14</td>
<td>Medium naphtha</td>
<td>Hot water ($\geq$50 °C), NaOH, CO$_2$ injection</td>
<td>(Foght et al. 2017)</td>
</tr>
<tr>
<td>Imperial Oil</td>
<td>Kearl</td>
<td>~10</td>
<td>Paraffinic</td>
<td>High temperature (70-90 °C) paraffinic treatment</td>
<td>(Oil Sands Magazine, 2021)</td>
</tr>
</tbody>
</table>

There are difficulties in predicting and modelling the diffusion of naphtha and other diluents from bitumen to the aqueous phase (Shafieiyoun & Thomson, 2018). Significant challenges involve biogenic
GHG emissions, including measuring the emissions from the pond’s surface to the wide range of diluents and extraction processes (Small et al. 2015).

2.2.4.3 Emissions Measurement

There are challenges in measuring GHG emissions from OSTPs. An emission isolation flux chamber is most commonly used (Figure 2.1) yet can have an accuracy range of 50-124% (Klenbusch, 1986). In addition, due to the large surface areas of the oil sands tailings ponds, covering a cumulative 220 km², it is not feasible to measure emissions over its entire surface (Alberta Environment and Parks, 2020). Furthermore, emission rates vary with respect to the location of the pond, within the ponds, the time of year, the weather and other factors (Dompierre et al. 2016). However, emission reports are comparable between ponds due to the Alberta Environment and Sustainable Resource Developments “Technical Guidance for Completing Specified Gas Compliance Report,” which has a standardized measurement protocol (AESRD, 2014).

![Figure 2.1: Schematic of an emission isolation flux chamber measuring gas emission rates from surfaces. Adapted from (Klenbusch, 1986).](image-url)
2.2.4.4 Biodegradation

Aerobic metabolism occurs at the surface and the top layer of the oil sands tailings ponds. However, due to the larger proportions of FFT and MFT with respect to PA pore water, anaerobic metabolism dominates (Foght et al. 2017). This degradation is characterized by decreasing BTEX (primarily from naphtha diluent) concentrations as pond depth increases. Aerobic degradation at the surface, followed by anaerobic degradation in the FFT and MFT, targets the easier-to-degrade lighter molecular weight components leaving higher concentrations of heavier and more recalcitrant compounds (Stasik et al. 2015). Methanogenesis dominates in Syncrude, Albian Sands and CNRL ponds. In contrast, sulphate reduction may dominate in Suncor ponds 5 and 6 and Syncrude’s CT fen reclamation site where gypsum (calcium sulphate) is added to consolidate MFT solids (Stasik et al. 2015).

Long lag times before methane production may be the time required for sulphate to be depleted in the MFT pore water resulting in methanogenic activity such that CH₄ emissions are observed in these ponds (Clemente & Fedorak, 2005). It was found that microbes slowly anaerobically degrade smaller organics but not high molecular weight polycyclic aromatic hydrocarbons (Folwell et al. 2016). It is hypothesized that biological activity could be limited by the diffusion of diluents (naphtha) from bitumen to the aqueous phase (Burkus et al. 2014). The difficulties in predicting and modelling this behaviour have been the focus of past and present research in contaminated groundwater systems (Shafieiyoun & Thomson, 2018). Mass transfer limitations could significantly impact understanding the emission rates, and until its attributes are known, a complete model of emissions will be difficult.

2.3 Characterization of Tailing Ponds

The chemical characteristics and microbial population of OSTPs vary with depth. Each tailing pond can have unique characteristics and hence different biological populations, but some trends are comparable between tailing ponds (Dompierre et al. 2016).
A wide range of microorganisms exist within OSTPs that can metabolize chemicals such as O₂, CO₂, CH₄, SO₄, H₂S, iron, manganese, Na, K, Cl, Ca, Mg, nitrogen, bitumen, and naphtha, consequently significantly affecting the pond’s chemical composition (Dompierre et al. 2016; Foght et al. 2017). However, differences in temperature, pH and Eh with respect to depth are not significant; density of solids consistently increases with depth (Dompierre et al. 2016; Small et al. 2015).

2.4 Biodegradation Studies

2.4.1 Bitumen Degradation

Some microbial populations use the lighter components of bitumen and naphtha as carbon substrates (Stroud et al. 2007). These specific degraders are in the aqueous phase near the NAPL or are at the aqueous/NAPL interface (Foght et al. 2017). Therefore, the mass transfer rate of bitumen/naphtha components from the NAPL to the aqueous phase is of interest in the degradation of bitumen/naphtha.

The biodegradability of naphtha and bituminous components has been demonstrated. For example, indigenous microbes from the FFT in Base Mine Lake (BML) were used as an inoculum in the aerobic degradation of bitumen as a carbon substrate, with and without bio-stimulation with acetate (Yu et al. 2018). However, most bitumen within tailing ponds is under anaerobic conditions (Dompierre et al. 2016).

Anaerobic microorganisms show potential for the biodegradation of higher molecular weight hydrocarbons. They include methanogens and other bituminous/naphtha degraders that are found in the subsurface of oil-sands deposits and the sediments of local rivers (adhered to the surface of bitumen globules) and consequently in oil sands process-affected tailing ponds (An et al. 2013; Wyndham & Costerton, 1981a, 1981b).

2.4.2 Labile Component Studies

Using enrichment cultures from Albian MFT, methanogenesis was found to co-occur with rapid nitrogen fixation when N₂ was present, suggesting fixation occurs in situ in OSTP (Collins et al. 2016). However, in the absence of this fixation, methanogenesis still occurred at the same rate, and other nitrogen sources
did not impact methanogenesis or nitrogen fixation. In addition, CH$_4$ production was increased with citrate, and the lag phase was reduced with additional nitrogen (Collins et al. 2016).

Most theoretical methods of estimating anaerobic methane production overestimate methane yields when the substrate biodegradability needs to be considered (Labatut et al. 2011). A wide range of complex carbon substrate mixtures was studied, and substrates with higher oil/lipid content had higher biogenic methane production, while more recalcitrant materials did not (Labatut et al. 2011). Methanogenic degradation of n-alkanes (n-hexane, n-heptane, n-octane and n-decane) (common components of naphtha) was studied in MFT microcosms over a 29-week incubation (Siddique et al. 2006). 20-100% of the n-alkanes were mineralized, with the highest mineralization occurring in the heaviest MW alkanes and decreasing mineralization with decreased MW and increased with acetate addition (Siddique et al. 2006).

In MFT microcosm studies with naphtha and BTEX compounds (key constituents of naphtha) under methanogenic conditions, low ratios of naphtha were mineralized, with only 15-23% of all compounds degraded after 46 weeks (Siddique et al. 2007). Toluene was the most degraded of the BTEX compounds, followed by o-xylene, m and p-xylene, and ethylbenzene. While the n-alkanes were degraded in similar trends to the n-alkane study, the heavier compounds (e.g., iso-paraffins and naphthalene) showed no degradation over 46 weeks (Siddique et al. 2007).

2.4.3 Long-Term Recalcitrant Degradation Studies

Zero and first-order kinetic models were used to predict CH$_4$ gas generation in MFT microcosms that were amended with naphtha and pure n-alkanes or BTEXs found in naphtha, with a high correlation (Siddique et al. 2008). However, when the model was extended to estimate gas production in MLSB, the projections were high (8.9-400 million L of CH$_4$/day) compared to the predictions based on in-situ pond surface measurements (3-43 million L of CH$_4$/day), indicating further work is required to understand better and predict GHG emissions from OSTPs (Siddique et al. 2008). Long-term studies were performed to determine the biodegradability of less labile and more recalcitrant organics using five iso-alkanes and three cycloalkanes over a 1700 d incubation with and without an MFT enrichment culture (Siddique et al. 2020).
Four iso-alkanes were completely mineralized (Siddique et al. 2020). Results indicate that MFT augmented hydrocarbon biodegradation under methanogenic conditions (Siddique et al. 2020).

The long-term methanogenic studies as above were continued ranging from one to seven years to be more comparable to the period of MFT incubation in the OSTPs (Siddique & Kuznetsova, 2020). The microorganisms sequentially and preferentially degraded certain hydrocarbons. The products of this metabolism altered the porewater and solid phase chemistry such that tailings de-watering and consolidation were accelerated (Siddique & Kuznetsova, 2020). Using these results, a stoichiometric and mathematical model was developed to predict GHG emissions from tailing ponds (Siddique & Kuznetsova, 2020).

Experimentally derived CH₄ production rates from incubations of oil sands tailings ponds with relevant organic were used to create databases, which in turn were used to generate an empirical model for CH₄ production (Kong et al. 2019). This was significant as degradation kinetics from long-term studies were considered for 18 relevant hydrocarbons and three (3) different oil sands operators, lag times, limiting nutrients, microbial growth and death (Table 2.2).

### 2.5 Naphtha Diffusion

The diffusion of biodegradable naphtha from within bitumen to being bioavailable in the aqueous phase is important for this research. There have been numerous studies performed and models generated for similar
systems. While much of the research discussed in this section does not directly relate to naphtha, OSTPs or bitumen, the methods used, and conclusions drawn could inform decisions on research interest.

2.5.1 Effect on Microbial Activity

The diffusion of biodegradable hydrocarbons (e.g., naphtha) from within bitumen to being bioavailable in the aqueous phase or at the bitumen/aqueous phase interface can affect in-situ biodegradation in OSTPs.

In a water/NAPL system, di(2-ethylhexyl)phthalate (DEHP) was mineralized more rapidly when dissolved in water than in a NAPL such as cyclohexane, hexadecane or dibutyl phthalate (Ortega-Calvot & Alexander, 1994). Furthermore, it was shown that when the substrate was in the NAPL, the biodegradation rates were higher if the microorganisms were in direct contact with the water/NAPL interphase (Ortega-Calvot & Alexander, 1994).

In another example, naphthalene was sorbed onto soil (Mihelcic & Luthy, 1991). Hence the aqueous naphthalene concentration depended on the sorption-desorption equilibrium, which was rapid compared to naphthalene degradation under denitrifying conditions. This information was used to model degradation; however, it was assumed that solute release to the aqueous phase was fast compared to the intra-NAPL (soil) diffusion (Mihelcic & Luthy, 1991). Intra-NAPL diffusion and other mass transfer effects of naphtha and bitumen must be better understood to validate this assumption under various conditions.

The interactions between bitumen and solvents were observed using NMR and X-Ray CAT technology (Wen & Kantzas, 2005). They determined diffusion coefficients for three bitumen-like NAPLs and six solvents. All combinations resulted in the same order of magnitude of diffusion coefficient (10^-6 cm^2/s).

2.5.2 Mass Transfer Models

In many cases, the bioavailability of hydrophobic organic solvents to microbes in two-phase systems may limit the degradation rate (Yang et al. 2009). For example, with increased soil organic content, bacterium-mineralized aqueous phenanthrene faster than dissolution could restore the aqueous concentration (Yang et
Hydrodynamic theory has been applied to multicomponent diffusion of non-associating systems (Kett & Anderson, 1968). Based on a generalized Fick’s law, including the effects of intramolecular interactions, diffusion coefficients were determined for each component in a dodecane-hexadecane-hexane and a toluene-chlorobenzene-bromobenzene ternary system (Kett & Anderson, 1968).

The mass transfer of polycyclic aromatic hydrocarbons (PAHs) from various NAPL phases into an aqueous phase was studied in batch and flow-through experiments ranging from several months to over a year (Ortiz et al. 1999). It was concluded that mass transfer was limited by the NAPL phase (as opposed to the aqueous phase resistance) when the NAPL had a high viscosity (Ortiz et al. 1999). An advancing depleting-zone model explained this result, where PAHs diffused across the NAPL-aqueous interface (Figure 2.2), leaving a localized area of lower PAH concentration within the NAPL phase (Figure 2.3). Hence with high viscosities, the rate of intra-NAPL diffusion limits the dissolution of PAHs into the aqueous phase, while the NAPL-aqueous interface limits dissolution with low NAPL viscosities (Ortiz et al. 1999).

Figure 2.2: Schematic of the release of organic hydrocarbons from a NAPL to an aqueous phase in a two-dimensional geometry. (a) The aqueous/NAPL interface shows concentration profiles in each boundary layer. the progression of a depleted zone in the NAPL phase is shown over time in (b) and (c). Adapted from (Ortiz et al. 1999).

Multicomponent intra-NAPL diffusion in aqueous-to-NAPL phase mass transfer was studied experimentally and computationally. It showed that intra-NAPL diffusion coefficients were most impacted
by the molecular weight of a compound, and the overall NAPL composition followed the NAPL phase viscosity (Shafieiyoun & Thomson, 2018). The viscosity of the bulk NAPL phase also strongly impacted mass transfer rate coefficients, where high viscosities resulted in low mass transfer coefficients and intra-NAPL diffusion coefficients. The radial model was used with intra-NAPL diffusion coefficients for each component, and mass transfer rates across the aqueous/NAPL interface used mass transfer coefficients for each component (equations as depicted in Figure 2.3). The same phenomena from the radial model in Shafieiyoun & Thomson, 2018 was considered in this work, however the physical geometry was a bitumen disc or cylinder with only a one flat face in contact with the aqueous phase instead of a three-dimensional sphere surrounded by an aqueous phase. Consequently, this can be simplified into a two-dimensional mass transfer problem.

Figure 2.3: Schematic depicting intra-NAPL diffusion which was simulated. The physical system depicted is the one studied in this work; a bitumen or NAPL disc at the bottom of an aqueous volume of water with only a two-dimensional interface between the NAPL and the water. Adapted from (Shafieiyoun & Thomson, 2018)
Also shown is the numerical representation of the system model by (Shafieiyoun & Thomson, 2018) (a spherical NAPL blob suspended in an aqueous solution in equation (2.1)).

\[
\frac{\partial C_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \sum_{j=1}^{n-1} D_{ij} \frac{\partial C_j}{\partial r} \right)
\]  

(2.1)

where \( r \) (mm) is the radial distance from the centre of the NAPL blob, \( C_i \) is the concentration (mg/L) of a component \( i \) within the NAPL blob, \( n \) is the number of components within the NAPL blob, and \( D_{ij} \) is the diffusion coefficient of component \( i \) in component \( j \) (Bird, 2002). The expression for flux across the aqueous/NAPL interface is described in equation (2.2) (Weber Jr. & DiGiano, 1996).

\[
J_i = \lambda_i (C_{eq,i}^W - C_i^W)
\]  

(2.2)

where \( J_i \) is the flux of component \( i \) across the aqueous/NAPL interface (mg/L/day) \( \lambda_i \) is the lumped mass transfer rate coefficient (1/day), \( C_{eq,i}^W \) is the concentration of each organic compound in the aqueous phase (mg/L), and \( C_i^W \) is the aqueous equilibrium concentration of each organic compound.

Another factor to consider when studying the mass transfer of organic compounds from a NAPL to an aqueous phase is the formation of interfacial films (Nelson et al. 1996). Coal tar-aqueous systems can create a semi-gelatinous interfacial film between the two phases after ~1 month of aging. The films have a comparable chemical composition to the bulk coal-tar phase, except for a significant water content and a higher viscosity. These films may limit the mass transfer between the two phases (similar to a thin emulsion layer).

The overall film mass transfer coefficients of nine PAHs were determined experimentally from a dense non-aqueous phase liquid (DNAPL) to an aqueous phase. Four batch equilibrium experiments were run in which various mole fractions of each PAH were placed in a sealed glass container with separate NAPL and aqueous phases, each with its own mixer and a consistent interfacial surface area. The
equilibrated aqueous phases were analyzed by HPLC (Mukherji et al. 1997). Film transfer coefficients were obtained using fugacity ratios, modified Raoult’s law and other thermodynamic theories. It was found that there were no significant trends in the overall film mass transfer coefficient of PAH components with respect to their mole fractions in the NAPL phase (Mukherji et al. 1997).

Modelled analysis of PAH release from a NAPL to the aqueous phase was performed (Peters et al. 1999). Due to complications in tracking individual PAHs and the dependence of PAH behaviour on the NAPL phase, a lumped mass transfer model can describe organics’ diffusion from a NAPL to an aqueous phase (Peters et al. 1999). This simplified model using a lumped mass transfer rate coefficient flux model equation (2.2) would be beneficial in determining if the mass transfer is limiting biodegradation in a system. Combining the first-order biodegradation term and the lumped mass transfer in equation (2.2) results in the generalized relationship of Equation (2.3) (Shafieiyoun & Thomson, 2018).

\[
\frac{\partial C_i^W}{\partial t} = \lambda_i (C_{eq,i}^W - C_i^W) - k_i C_i^W
\]  

(2.3)

where \( k_i \) is the first-order biodegradation reaction rate coefficient (1/day), \( C_i^W \) is the concentration of each organic compound in the aqueous phase (mg/L), and \( C_{eq,i}^W \) is the aqueous equilibrium concentration of each organic compound (Shafieiyoun & Thomson, 2018).

2.6 Unified Model

The combined effects of mass transfer and biodegradation ultimately lead to the biogenic production of gases in the oil sands tailings ponds. A singular unified model would prove invaluable moving forward to predict emission rates, the effects of possible treatments and more.

A model was made in PHREEQC (Parkhurst & Appelo, 1999), an open-source geochemical program, to simulate the anaerobic degradation of soil organic carbon in the Artic tundra (Zheng et al. 2019). While the model has simplifications of the geochemical impacts on microbial decomposition, it
includes the thermodynamic impacts on microbial growth via methanogenesis, fermentation and iron reduction, upstream carbon transformations and sources, and humic ion-binding used for pH simulation for various redox conditions in soils for various means of carbon decomposition (Zheng et al. 2019). In addition, it accurately simulated the CO₂ production on less recalcitrant carbon pools in the Artic tundra (Zheng et al. 2019). Furthermore, a PHREEQC model predicted biomass growth and decay rates of two different in-situ uranium reduction field experiments (Istok et al. 2010). Finally, a coupled model of terrestrial water, carbon, and nitrogen dynamics successfully predicted site-level woody and herbaceous vegetation respiration rates (Thornton & Rosenbloom, 2005). While not applied to oil sands tailings ponds, the versatility and successful application of a wide range of theoretical equations show that a PHREEQC model could model biogenic gas production in OSTPs.

A Community Land Model and Windermere Humic Aqueous Model were modified to include carbon and nitrogen cascade decomposition, organic substrate turnover, fermentation Fe (III) reduction, and methanogenesis (Tang et al. 2016). They were proven accurate when tested with Artic tundra soil-based microcosm tests (Tang et al. 2016). In addition, the effects of water saturation, pH and temperature on methanogenesis were also considered with simplified equations (Xu et al. 2015). The resulting simulations and their comparisons to incubation experiments with permafrost soils showed that using the simplified equations retains much efficacy (Xu et al. 2015).

Finally, a vertical component to carbon and nitrogen pools was added to Community Land Model along with other additions of alternative soil decomposition cascades and separate modelling of NO₃⁻ and NH₄⁺ in the nitrogen cycle (Koven et al. 2013). However, the additions yielded limited success compared to various site-level observations, indicating that care must be taken when adapting such models for various applications (Koven et al. 2013).

2.7 Conclusions and Next Steps

Various studies have documented the conditions and compositions of the oil sands process affected tailings ponds, such that a similar water mixture can be replicated. Due to the toxicity of bitumen and naphtha
hydrocarbons, the biogenic gases produced, and regulations to reclaim land and tailings waste, understanding the biodegradation of the hydrocarbons is of great interest. While many organics can be degraded, more labile components are degraded in less than a year in microcosm experiments. Specific degraders are hypothesized to exist in the aqueous phase or at the aqueous/NAPL interface; hence the mass transfer of hydrocarbons from the bitumen to the aqueous phase within the MFT could be limiting in-situ degradation in the oil sands tailings ponds. Various models are viable in describing and predicting multicomponent interphase diffusion, intra-NAPL diffusion, and film formation based on various parameters. However, as the composition of bitumen and the aqueous phase are complex, a predictive model would likely result in inaccurate mass transfer rates; hence a system-specific empirical study will be required to gain further insight into the process.

Furthermore, the effect of nutrient availability, electron acceptors, temperature, pH and other factors greatly impact the ability of the microbial cultures to degrade the hydrocarbons of concern and emit GHGs such as CH₄ and CO₂. While empirical data is required to understand much of these phenomena due to the variability between and within these tailing ponds, pre-existing models supplemented with empirical data from microbial and mass transfer experiments could be beneficial in modelling the biogenic gas emission rates from oil sands tailing ponds, predicting the effects of value uncertainty, and predicting the results of possible treatments (e.g., bio-stimulation).

2.8 References


An, D., Caffrey, S. M., Soh, J., Agrawal, A., Brown, D., Budwill, K., Dong, X., Dunfield, P. F., Foght, J.,


Siddique, T., & Kuznetsova, A. (2020). Linking hydrocarbon biodegradation to greenhouse gas emissions


Hydrocarbons and In Situ Colonization of Bitumen Surfaces Within the Athabasca Oil Sands Deposit. In Applied And Environmental Microbiology. https://doi.org/10.1128/aem.41.3.791-800.1981


Chapter 3

Fluorescence Spectroscopy Analysis of Solubilized Aromatic Naphtha Surrogates

Abstract

The greenhouse gas (GHG) emissions from the Athabaska oil sands tailing ponds (OSTPs) are an environmental concern due to the CO₂ and CH₄ emissions from the biodegradation of naphtha diluent. Experiments performed with mature fine tailings (MFT) indicated limitations in the rate of naphtha degradation due to the bio-accessibility of naphtha solubilized within the bituminous phase. However, this phenomenon is difficult to study since there is no easy method to measure naphtha.

Current methods to quantify naphtha composition are costly, time-consuming, or unfeasible to perform frequently. Hence, a cheap, reliable, and rapid fluorescence spectroscopy method was developed with sufficient precision and accuracy to determine the concentrations of naphtha surrogates (o-xylene and 1-MN) in the aqueous phase of MFT. A single wavelength steady-state excitation at 260 nm and emission wavelength scans of 270-410 nm were sufficient for quantifying o-xylene and 1-MN. The method was optimized for 10:1 molar ratios of o-xylene:1-MN as they were expected in the applications of concern. The addition of high-performance liquid chromatography (HPLC) grade MeOH (20 vol.%) as a co-solvent to aqueous samples reduced naphtha volatilization sufficiently until analysis could be performed. Experiments also showed that a saline (simulated aqueous OSTP pore water) phase and soluble bituminous constituents can impact fluorescence analysis. Different surrogate ratios, the presence of salts and bitumen were corrected for by using appropriate calibration curves.

Repeated extractions of MFT samples with Reverse Osmosis (RO) water and 20% HPLC grade MeOH followed by fluorescence analysis of the supernatant can be used to determine the relative changes in naphtha surrogate concentrations and the partition coefficients for naphtha surrogates between aqueous and non-aqueous phases in specific MFT samples.
3.1 Introduction

The Canadian Athabascan oil sands (142,200 km²) are one of the world’s largest petroleum reserves (Small et al. 2015). In 2011, an estimated 33,100 tons of CH₄ and 423,000 tons of CO₂ were emitted from the Suncor, Syncrude, and Shell Albian OSTPs in the Athabascan region which accounts for 0.65% of the industries GHG emissions in the oil sands sector in Alberta (Baray et al. 2018; Siddique et al. 2017; Oil Sands Discovery Center (OSDC), 2023). In the commonly employed Clark’s hot water extraction process (CHWEP), oil sands ore from open-pit mining is crushed, and mixed with hot water and NaOH, forming an unstable slurry from which the bitumen product is separated from the solids and aqueous waste (Rao and Liu 2013). This waste contains bitumen in which some naphtha diluent is solubilized (Penner and Foght 2010). Naphtha is a mixture of primarily ~C5-C16 aliphatics, monoaromatics (benzene, toluene, ethylbenzene and xylenes (BTEX)), and naphthalene (Speight 2019; Siddique et al. 2007). Constituents of naphtha (and bitumen) can be consumed anaerobically by microbes in the OSTPs leading to GHG emissions. While increased naphtha concentrations can increase GHG emissions to a degree, the bioavailability of naphtha in the aqueous phase is hypothesized to be rate-limiting (Foght, Gieg, and Siddique 2017; Ramsay et al. 2021). Consequently, the analysis of naphtha in the aqueous phase is important to understand the mass transfer behaviour of naphtha between the bitumen and the aqueous phases in mature fine tailing (MFT). As the variety and complexity of naphtha’s constituents can make analysis difficult, the system may be simplified using specific constituents or “naphtha surrogates” that are representative of the major groups of compounds within naphtha. This can result in higher and easier-to-measure signals in a variety of analytical methods. The use of select coal-tar constituents or “surrogate” chemicals has been successful in the study of hydrocarbon diffusion from coal-tar residues (Shafieiyoun & Thomson 2018).

An analytical method was needed to track the concentrations of naphtha surrogates in the aqueous phase. Gas chromatography (GC) with flame ionization detection (FID) or mass spectrometry (MS) were investigated for the analysis of naphtha as it is used for hydrocarbon analysis of MFT and requires the
analytes to be stable and solubilized in an analytically clean non-aqueous phase (Mackay et al. 1982). However, there are challenges faced with extracting naphtha into the solvent of interest, such as methyl-ethyl-ketone (MEK) and hexanes (Whitley & Thompson 2022; Laborde-Boutet 2018) or solid phase microextraction (SPME) with a siloxane polymer (Moe 2021; Kataoka et al. 2000; Górecki 2002).

A MEK extraction method was developed by COANDA (Research and Development Corporation Edmonton Alberta) to determine MFT naphtha content. In the method, 1:5 MFT:MEK weight ratio mixtures (1,000 mg/L n-hexadecane as an internal standard) were shaken for 2 min, settled for 16 h and then extracted MEK was filtered before GC analysis. MEK can extract lighter naphtha hydrocarbons without creating an emulsion with the bitumen (Laborde-Boutet 2018; Moe 2021). However, this extraction method takes a long time (30-48 hrs), is expensive, and is only optimized for bituminous/aqueous multiphase samples.

Hexane extraction was developed with the Queen’s Analytic Services Unit to determine aqueous naphtha surrogate concentrations. In this method, a 1:10 hexane: aqueous sample was shaken for 2 min, settled for 15 min, and the hexane was recovered for GC-FID analysis (50 µL of a 1920 mg/L naphthalene-d8 (d8N) in neat MeOH as an internal standard) (Whitley & Thompson 2022). Inconsistencies with the extraction efficiency and limits to solvent ratios (based on GC minimum injection volume) yielded unacceptable results.

The third extraction method was developed by Moe (2021), where a siloxane (polydimethylsiloxane) polymer rod is inserted into a multiphase OSTP sample to absorb naphtha. The rod is removed after 24 h, and the sorbed components are desorbed in HPLC grade ethanol (EtOH) for 6 h (Moe 2021; Kataoka et al. 2000). Partition coefficients between the siloxane polymer and all phases were used to derive a multiphase fugacity equilibrium model, which predicts equilibrium conditions with varying initial naphtha concentrations and ratios of bitumen, water and headspace volumes (Mackay & Paterson 1981). Shortcomings include the duration of the method (≥36 hr) and the reliance on two extractions, which can vary in efficiency, making analytical minimum detection limits (MDLs) important (Moe 2021).
In an attempt to reduce costs compared with GC methods (up to $200/sample with a 1 h run time), previous iterations of work in this thesis replaced hexane and H₂ with MEK and He, respectively (Whitley & Thompson 2022). While similar retention times and accuracy (for toluene, o-xylene, nonane, d8N, and 1-MN) were achieved, the MDLs and consistency of the extractions were insufficient for our work.

With these complications, an alternative analytical method was required. UV-vis was a potential alternative, as well as fluorescence spectroscopy which can be ~50 times cheaper and faster than GC (Moe 2021). While both were promising, due to time constraints and limited covid-19 related equipment access, fluorescence spectroscopy was chosen for further investigation. Fluorescence occurs when a molecule absorbs photons, exciting one of the molecule’s electrons to an elevated energy state which then rapidly loses thermal energy due to molecular vibrations, and then emits photons when returning to the original ground-state (Lakowicz 2006; Baszanowska & Otremba 2017). Energy can also be lost to the surroundings and through non-radiative pathways. Emitted wavelengths are longer than the original excitation wavelength (“Stokes shift”) (Lakowicz 2006; Baszanowska & Otremba 2017). The dissipation of absorbed energy often occurs such that the wavelength of photons emitted from the fluorescent molecules are independent of the excitation wavelength. Fluorescence occurs for a variety of compounds yet is commonly observed in aromatics. Naphtha contains many aromatic hydrocarbons making it ideal for fluorescence spectroscopy (Lakowicz 2006).

The quantum yield is the ratio of photons emitted by a fluorophore to the number of photons absorbed (Lakowicz 2006). Higher quantum yield fluorophores have better MDLs and resolution at lower concentrations; however, they can also have lower linearity at higher concentrations (Lakowicz 2006). Fluorescence quenching can occur from the presence of salts which reduces the quantum yield of a fluorophore by forming complexes providing more non-radiative pathways for energy to dissipate. In the case of multiple fluorophores with broad emission spectra, their fluorescence spectra can overlap, effectively decreasing the sensitivity of the method (Lakowicz 2006). The presence of random molecules in solution can absorb light which affects the spectral overlap. Steady-state fluorescence spectroscopy is
commonly used, applying constant excitation light to a sample and measuring the emission spectrum over all wavelengths during this time (Lakowicz 2006).

The primary goal of this research was to develop an analytical method to study the mass transfer behaviour of naphtha in MFT between its non-aqueous and aqueous constituents (Chapter 4). However, this was difficult due to the complexity of naphtha, bitumen, MFT’s solids and aqueous phases. Hence simplifications were made to increase the feasibility of the analysis while still providing insight into the mass transfer phenomena occurring within the MFT of the OSTPs. Consequently, work in this chapter focused on the development of an analytical method to track the mass transfer of naphtha surrogates from cleaned bituminous phases to aqueous phases, requiring sufficient performance (sensitivity to ~1 mg/L) in the presence of salts and MFT/bitumen.

Naphtha and bitumen contain one and two-ring aromatic hydrocarbons and many non-fluorescent compounds. Since the differentiation between their fluorescent signals is difficult (not discernable with 0-1 wt.% naphtha in MFT using SPME) (Moe 2021), the use of single compounds that are representative of naphtha (naphtha surrogates) was chosen for a higher emission response, in the development of this method (Lakowicz 2006). Furthermore, due to the wide compositional range and non-homogeneity of bitumen found in OSTPs, protocols were used to obtain a “cleaned” bitumen for reliable study in this method development.

This new method must (1) be used to select naphtha surrogates that have a low MDL and strong linearity; (2) accurately and precisely determine aqueous naphtha surrogate concentrations; (3) not be significantly impacted by interference between naphtha surrogates or the organics from bitumen and MFT samples, and finally (4) be a simple protocol.
3.2 Materials and Methods

3.2.1 Fluorescence Spectroscopy Methodology

The fluorescence spectrophotometry protocol developed in this study was based on work by Moe (2021) which was proven to measure naphtha concentration changes of ~1,000-2,000 ppm within an entire sample in the presence of bitumen and MFT (with the use of solid-phase micro-extraction, which included dilutions) (Moe 2021). This study used a PTI QuantaMaster 400 spectrometer (75 W xenon arc lamp, excitation and emission monochromators and a photomultiplier detector) was turned on ≥ 30 min prior to its use to achieve a stable lamp temperature. The method also used 6 nm slits, and fluorescence responses were measured at 1 nm increments with a 0.3 s integration time using PTI FelixGX Software. A standard solid anthracene-naphthalene block was first used after the equipment warmed up (Moe 2021).

Modifications to this method included a blank of 20% HPLC grade MeOH in Reverse Osmosis (RO) water, and 3-point calibration curves of o-xylene and 1-MN (in a 20% HPLC grade MeOH solution) to calibrate the device. While HPLC grade EtOH was used previously (Moe 2021), it was replaced with HPLC grade MeOH. Similar to Moe 2021, prior to analysis, samples were vortexed for 30 s, and 3 mL was pipetted into a 1 cm quartz cuvette, covered, and wiped clean with a Kimwipe before insertion into the spectrometer. In this work, small portions of experimental samples were removed and analyzed to minimize volatilization and to find the appropriate analytical dilution. Samples were excited at 260 nm. However, for o-xylene and 1-MN, emissions were measured at 270-410 nm. The cuvette was rinsed twice with RO water and MeOH in between samples.

Additional work was needed to (1) establish fluorescence background signals associated with bitumen, (2) determine the detection limit of the naphtha surrogates and the linear calibration range, and (3) evaluate the potential for fluorescence analysis with MFT samples to track biodegradation over time as suggested for future work (Moe 2021). (1) and (3) are dealt with in Chapter 4, and (2) was approached by limiting the choice of naphtha surrogates, solvent, and length of time between sampling and analysis in this chapter.
3.2.2 Selection of Naphtha Surrogates

A select few naphtha constituents (referred to as “naphtha surrogates”) were investigated for use in fluorescence spectroscopy. The use of two fluorescent surrogates could increase detectability (for the same quantity of analyte) in the presence of bitumen by representing the lighter and heavier constituents of naphtha. For the lighter constituents, toluene and o-xylene were studied, while anthracene and 1-MN were studied for the heavier constituents. Toluene, o-xylene and 1-MN were analyzed with an excitation wavelength of 260 nm and anthracene at an excitation wavelength of 310 nm. All were within the 270-410 nm emission range (Moe 2021). The fluorescence response spectra and calibration curves for these surrogates were generated.

3.2.3 Effect of Methanol (as a co-solvent) on minimizing loss of surrogates

Many constituents of naphtha, such as xylenes, have high vapour pressures (1,100 – 1,170 Pa at 25°C), moderate solubilities (160 – 220 mg/L at 25°C), can be highly volatile in water (smelt in nearby air when in water at 0.53-1.1 mg/L) and have short half-lives in still water (5.6 hr in 1 m deep water exposed to the open atmosphere at 25°C) (Centers for Disease Control and Prevention 2019; Mackay et al. 2013; Government of Canada 1993; Mackay & Wolkoff 1973). The shallow depth and agitation experienced in lab-scale sample manipulation could result in short (<5.6 hr) half-lives. Consequently, the stability of naphtha surrogates in solution must be sufficient such that there are no significant losses between sampling and analysis due to the high volatility of the naphtha surrogates. Hence a co-solvent of HPLC grade MeOH was used to stabilize the samples, as alcohols increase the miscibility of naphtha-like organics in solution (Centers for Disease Control and Prevention 2019). To determine the effect of increasing MeOH concentration on fluorescence, ~1 g bitumen droplets were placed in scintillation vials filled with 20 mL of 0, 1, 10 or 20% (vol/vol) MeOH in RO water. The aqueous phases were removed after 1d (without disturbing the bitumen droplet) and spiked with o-xylene (100 µg/L, 1 mg/L, 10 mg/L, and 100 mg/L)
and/or 1-MN (10 µg/L, 100 µg/L, 1 mg/L, 10 mg/L). Background signals were obtained from negative controls (i.e., without o-xylene or 1-MN).

### 3.2.4 Interference between surrogates (o-xylene and 1-MN)

When performing fluorescence spectroscopy to analyze more than one compound (especially with a single wavelength excitation), it is possible for the emission spectra of the analytes to overlap with one another, or fluorescence quenching could occur via a variety of mechanisms (e.g., resonance energy transfer (RET)) (Lakowicz 2006). When an experimental aqueous sample is saturated (with o-xylene, 1-MN and background aqueous soluble bituminous compounds), o-xylene and 1-MN are present in experimental aqueous samples at an ~10:1 molar ratio (to be expected with pure component solubilities of 178.5 and 28.5 mg/L for o-xylene and 1-MN respectively). This and other ratios were tested by comparing the fluorescence spectra for solutions of 1 mg/L o-xylene with 100 µg/L, 10 µg/L or 10 mg/L 1-MN in 20% MeOH.

### 3.2.5 Interference between naphtha surrogates and bituminous components

A source of interference in the fluorescence signals could occur between the naphtha surrogates and the aqueous soluble bitumen compounds. Other constituents of naphtha and bitumen have the same aromaticity as o-xylene and 1-MN, producing similar fluorescence signals (Speight 2019; Foght et al. 2017). Interference may also arise from fluorescence quenching and RET (Lakowicz 2006). To investigate this, bitumen droplets in the bottom of scintillation vials filled with RO water or simulated OSTP pore water were sealed, left in sessile contact, and stored in the dark for 1, 4 and 9 d before the aqueous phase was recovered (now referred to as “background” bituminous signals). A serial dilution of o-xylene and 1-MN in HPLC grade MeOH was spiked into the recovered aqueous phases with the “background” bituminous signals. All samples were at a final 1 vol.% MeOH and were analyzed within 2 d of storage. The results from these experiments were used to generate calibration curves.
3.2.6 Effect of solution salinity on fluorescence

The aqueous phase in MFT contains NaOH, other salts, and trace metals and could impact naphtha mass transfer (Foght et al. 2017). With compositional variability between and within OSTPs, the composition of three Athabascan OSTP samples were averaged to represent a “simulated OSTP pore water” with 0.025 mg/L NH₄Cl, 0.5484 mg/L NaCl, 0.5220 mg/L Na₂SO₄, and 1.3082 mg/L NaHCO₃. These samples originated from two OSTPs in the Athabascan region, are referred to as; Pond A or PA (samples taken from depths of 5 m and 15 m) and Pond B or PB (samples taken from a depth of 12.5m). Calibration curves of 10:1 molar ratio of o-xylene and 1-MN in (a) RO water, (b) RO water with 20% HPLC grade MeOH, and (c) simulated OSTP pore water with 20 vol.% HPLC grade MeOH were prepared.

3.2.7 Analysis of surrogates in MFT

To investigate interference from MFT, Pond A – 5 m, Pond A – 15 m, and Pond B – 12.5 m samples were diluted in a 1:4 vol/vol ratio in RO water with 2.0 vol.% naphtha surrogates. Samples were then centrifuged at 8,000 rpm for 20 min; the supernatant was recovered and analyzed. The remaining solids were then resuspended in solution, mixed, centrifuged, and the supernatant collected for analysis a total of five times.

After the five centrifugation steps (performed with triplicate samples), the remaining solids were pooled, air-dried in the fume hood for 24 h, ground, placed in pre-weighed beakers, and dried in an oven at 105 °C for 24 h (McKeague 1978). Beakers were reweighed after they cooled and placed in a preheated muffle furnace at 420 °C for 16 h to determine the total organic carbon in the sample (McKeague 1978).

3.2.8 Statistical analysis of surrogates

Statistical evaluation for significant differences between two data sets (or samples with error) was completed in two steps. First, a one-tailed F-test was used to determine if the variance of one data set (or sample) was greater or equal to the other. The F-test assumed normally distributed populations with random and independent data and used α-values of 0.05. If the F-test determined that the values were equal, a two-
sample equal variance T-test was performed. Otherwise, a two-sample unequal variance T-test was done. Additionally, in step two, the averages of the two data sets were compared. If they were similar, a two-tailed T-test was done in combination with the two-sample equal or unequal variance T-test. If the averages were different, a one-tailed test was used. Assumptions for the F-test and T-test were the same, and values that were determined as statistically significant were at α-values of 0.05.

3.3 Results and Discussion

3.3.1 Selection of Naphtha Surrogates

Aromatic compounds that are representative of the lighter (monoaromatics) and heavier (di- and triaromatics) constituents of naphtha (referred to as “naphtha surrogates”) were investigated for use in fluorescence spectroscopy (section 3.2.2).

Of the lighter monoaromatic surrogate candidates, toluene and o-xylene had similar fluorescence emission spectra (Lakowicz 2006) and experimental linearity over 1-50 mg/L and 100 µg/L-100 mg/L, respectively. O-xylene was chosen due to its slightly better linear response ($R^2 >0.999$ compared to 0.992 Figure A3.4) and the fact that toluene can be “analytically dirty” (Lewis Sr. 2004).

For the heavier constituents, anthracene is an exception to most common fluorescence patterns and had a phenomena with multiple peaks over 300-410 nm, while 1-MN has more symmetric and distinct emissions at 315-410 nm. Hence 1-MN was chosen with its strong linear signal ($R^2$ of 0.998) from 10 µg/L to 10 mg/L (Figure A3.1) (Lakowicz 2006). The surrogates yielded higher resolution and distinct peaks in MFT-affected aqueous samples compared to whole naphtha (Figure A3.4).

3.3.2 Selection of a Co-Solvent

In previous experiments, volatilization of the naphtha surrogates from RO water showed an average of 62% and 59% reduction in the fluorescence signal of o-xylene when the same samples were analyzed two and three consecutive times 5 min apart. Hence the addition of a co-solvent that is miscible in water
and can reduce naphtha volatilization was investigated (section 3.2.4) (Moe 2021; Centers for Disease Control and Prevention 2019). As alcohols increase the solubility of naphtha-like organics in solution, the co-solvents tested for this purpose were HPLC grade EtOH, reagent grade and HPLC MeOH, anhydrous EtOH, isopropanol, butanol and acetonitrile (Centers for Disease Control and Prevention 2019). HPLC grade MeOH was found to be the most promising and was investigated further.

### 3.3.3 Effect of MeOH Concentration and Sample Storage Time

To determine an appropriate amount of MeOH to add, ~1 g bitumen droplets were placed in scintillation vials filled with 20 mL of RO water. The aqueous phases were removed after 1 or 9 d to create “background” bitumen contamination (as would occur in the mass transfer experiments in Chapter 4). Then HPLC grade MeOH was added to the removed water to achieve 1, 10 or 20 vol.% solutions, then spiked with o-xylene or 1-MN before being stored for 0, 6 or 19 d. Background signals from negative controls (e.g., without o-xylene or 1-MN) were subtracted from spiked samples.

As seen in Figure 3.1, the fluorescence signals from the samples decreased over 6 and 19 d of storage by 40.0% and 68.9% for 0 vol.% MeOH, by 9.5%, and 29.2% for vol.1% MeOH, by 5.0%, and 20.5% for 10 vol.% MeOH, and by -7.3% and 12.7% for 20 vol.% MeOH. As individual sample errors were an average of 11%, these losses with MeOH added as a co-solvent were not significant for the 0-6 d, yet there were significant losses for 0-19 d based on a one-tailed, two-sample, equal variance t-test at a 95% confidence interval. The losses observed with MeOH were a significant improvement over the losses observed with no MeOH added. While only 10 mg/L o-xylene with 1 d of equilibration with bitumen is shown in Figure 3.1, the results are representative of both surrogates at different bitumen equilibration times (1-9 d).
Figure 3.1: Fluorescence of naphtha surrogates as a function of time after equilibration with bitumen for 1 d. A background signal was generated with samples in contact with bitumen. Once the bituminous aqueous sample was extracted, 0, 1, 10 or 20% MeOH and varying amounts of o-xylene and 1-MN were added, and samples were analyzed after 0, 6, and 19 days (n=3), and error bars are one standard deviation. The dotted lines indicate controls with no methanol.

To determine whether removing a sample for analysis could result in volatilization of naphtha surrogates, 20% MeOH solutions with o-xylene and 1-MN were repeatedly analyzed 5 min apart. Losses were similar to those found over the long-term (with some slightly larger losses from o-xylene see Figure A3.3), where losses were not significant from the first to the second analysis but were for the third. Hence, it can be concluded that samples are stable for at least 6 d but exposing samples to the atmosphere results in some volatilization.

3.3.4 Interference between Naphtha Surrogates

With a single excitation wavelength, there is potential for overlapping and/or interference between the emission spectra of the naphtha surrogates. 1-MN fluorescence responses do not appear to interfere with the o-xylene responses at low ≥ 1mg/L 1-MN concentrations in the o-xylene 270-300 nm integration range (Figure 3.2b). However, with a 1 mg/L o-xylene and 10 mg/L 1-MN concentration, the fluorescence signal is falsely high in the 300-315 nm range between the o-xylene and 1-MN emissions spectra used for analysis (see the arrow on Figure 3.2b and Figure A3.7b).
Figure 3.2: Fluorescence emission spectra of 1 mg/L o-xylene with 1-MN varying from 10 µg/L to 10 mg/L to test for the interference of fluorescence response when excited at 260nm. (a) Shows the entire emission spectra for both o-xylene and 1-MN from 270-410nm, with the integration region for o-xylene of 270-300 nm highlighted with a black box. While (b) shows a zoomed-in plot of the o-xylene emission range of 270-300 nm and a blue arrow indicating the falsely high signal in the 300-315 nm between the integrating ranges for o-xylene and 1-MN when one surrogate has a much higher concentration than the other.

In previous experiments, o-xylene and 1-MN are present in experimental aqueous samples at ~10:1 molar ratios (not dissimilar to the pure component aqueous solubilities of the o-xylene 1-MN which are 178.5 and 28.5 mg/L respectively or a ~6.3:1 ratio). The fluorescence signals behaved consistently at ~10:1 ratios; however, for ratios significantly below (e.g., ~1:1) o-xylene signals were affected by 1-MN. For ratios significantly above 10:1 (e.g., ~100:1) 1-MN signals were affected by o-xylene (Figure 3.2). Other ratios can still be quantified with this method. However, as it was designed for ~10:1 ratios, other ratios would need to be artificially controlled to be observed in solution, and new calibration curves for the ratios of interest would be required. These new calibration curves would likely result in smaller linear analytical ranges.

3.3.5 Interference between Surrogates and Bitumen

The presence of water-soluble bituminous compounds can interfere or overlap with naphtha fluorescence spectra as some constituents of bitumen have the same aromaticity as o-xylene and 1-MN (Shafieiyoun and Thomson 2018). The effect of bitumen in RO water was studied in solutions with 9 d
bitumen equilibration and then spiked with naphtha (Figure 3.3a). The “bitumen + naphtha” signal was larger than the sum of the individual naphtha and bitumen signals. This could indicate loss of naphtha components from RO water as naphtha components were possibly less volatile/more stable in the presence of bitumen as they may preferentially sorb to bitumen (Mihelcic & Luthy 1991). Additionally, the fluorescence emission response of a mixture is generally lower than the sum of the individual spectra when interference occurs (Lakowicz 2006).

When using 20% MeOH in RO water, the individual signals of naphtha and bitumen were much closer to the combined signal of a “bitumen + naphtha” mixture (Figure 3.3b). Furthermore, the naphtha only and bitumen + naphtha signals show distinct peaks at the 270-300 nm and 315-410 nm range, which correlate to mono- and di-aromatics, respectively. Hence it can be concluded that the naphtha signals can be distinguished from bituminous background signals when the concentration of naphtha is sufficiently high, and a correction is made for the background bitumen signal. A similar phenomenon was found in mixtures of naphtha, or MFT, or naphtha + MFT in water using a siloxane polymer for solid-phase microextraction into ethanol (Moe 2021).
Figure 3.3: The fluorescence emission spectra of preparations excited at 260 nm for (a) naphtha diluted in RO water, RO water in contact with a bitumen droplet for 9 d, and RO water in contact with a bitumen droplet for 9 d and spiked with 20,000 mg/L naphtha and, (b) naphtha diluted in RO water, RO water sample in contact with a bitumen droplet for 9 d, and RO water sample in contact with a bitumen droplet for 9 d spiked with 20,000 mg/L naphtha. All samples in “b” were stabilized with 20% MeOH.

HPLC grade MeOH (20 vol.%) was added to RO water from 1 d of equilibration with bitumen, then spiked with o-xylene and 1-MN to make calibration curves. O-xylene and 1-MN were found to be linear from 100 µg/L – 30 mg/L and 10 µg/L – 5 mg/L with R² values of 0.9912 and 0.9835, respectively.

3.3.6 Effect of Contact Time of Bitumen with Aqueous Phase

Several mechanisms between bituminous compounds and the naphtha surrogates can cause interference of the fluorescence signals. Background aqueous solutions from 0, 1, 4 and 9 d of contact with a bitumen droplet were used to investigate changes in fluorescence signals due to bitumen contact time. This resulted in increasing signals with increasing contact time. The largest increase at 320-345 to ~345-365 nm indicated an increase in multi-ring aromatics from bitumen, while the smaller increases in the 270-300 nm region related to the mono-aromatics found in bitumen (Figure 3.4a). Longer bituminous contact times not only changed the quantity of fluorescent contaminants (increased overall signal) but also the composition of the contaminants changed (e.g., a shift of signal peak), both of which could impact the fluorescence analysis of the naphtha surrogates.
Figure 3.4: Fluorescence emission spectra for aqueous samples from 1, 4, and 9 d of contact with a bitumen droplet. Plots show the (a) “background” or blank signals, which have no additional surrogates, and (b) signals where 100 mg/L o-xylene and 1-MN 10 mg/L were added to background samples. All samples were analyzed in a final 1% MeOH in RO water and excited at 260 nm.

More aqueous solutions with background bituminous compounds (1, 4, and 9 d of sessile equilibration with a 1 g bitumen droplet) were prepared, mixed with HPLC grade MeOH to achieve a 20% (vol/vol), then spiked with varying concentrations of o-xylene and 1-MN and analyzed after 2 h, 6 d, and 19 d of storage.

With 0% MeOH controls, there were significant decreases in concentration over time. With 20% MeOH, there were no significant decreases (two-tailed t-test, p>0.18) for any o-xylene concentration over the first 6 d (Figure 3.5a-b). 1-MN concentrations of 10 mg/L and 1 mg/L also showed no decreases in 0-6 d (Figure 3.5b) (p>0.087). 10 µg/L 1-MN was below minimum detection with any background bituminous contamination, while 100 µg/L was below the minimum detection for 9 d equilibration (t-test p-values of 0.0017-0.05). These losses are likely due to the volatilization of 1-MN or other constituents of bitumen with similar fluorescence spectra creating an effective minimum observed concentration for 1-MN. These similar losses were also likely occurring at high concentrations but had a limited impact on the overall signal. This data represents most of the experiments performed, and the naphtha surrogate concentrations shown are the most relevant for the mass transfer experiments in Chapter 4.
Figure 3.5: Fluorescence of naphtha surrogates as a function of time after equilibration with bitumen for 1 and 9 d. A background signal was generated with samples in contact with bitumen. Once the bituminous aqueous sample was extracted, 0, or 20% HPLC grade MeOH and varying amounts of o-xylene and 1-MN were added, and samples were analyzed after 0 days, 6 days, and 19 days (n=3), and error bars are one standard deviation. Dotted lines indicate controls with no MeOH, circle markers 1 d equilibration trials, and diamond markers 9 d equilibration trials. Plots with 0% and 20% MeOH are shown for o-xylene at (a) 100 mg/L and (b) 10 mg/L and 1-MN at (c) 10 mg/L and (d) 1 mg/L.

The bituminous contaminated aqueous solutions (0, 1, 4, and 9 d of bitumen contact) were used to create calibration curves for o-xylene:1-MN at a 10:1 ratio in 20% HPLC grade MeOH measured after 2 h of storage (Figure A3.6). While the overall signal increased (due to background signals), linearity was maintained with $R^2$ values of 0.9701-0.9873 for o-xylene and 0.9873-0.9980 for 1-MN (Figure A3.6). The o-xylene trials had the same linear ranges (0 – 100mg/L) and similar slopes (6.8x10^4 - 2.2x10^5 counts*nm/s/mg/L). The 1-MN trials also had the same linear ranges (0 – 10 mg/L) and similar slopes (3x10^6 – 4x10^6...
counts*nm/s/ mg/L). Hence in experiments involving bituminous contamination, control samples without naphtha surrogates could be analyzed, and their signal subtracted from those with the surrogates.

3.3.7 Effect of Salinity on Fluorescence

To investigate the effects of pore water salts, calibration curves were developed for o-xylene and 1-MN in a 20% HPLC MeOH simulated OSTP pore water solution containing the major salts in MFT such as NaCl, NaHCO₃ and Na₂SO₄. While salts were only tested at one concentration (the simulated OSTP pore water solution), its presence decreased the fluorescence signals for 1-MN at high concentrations and had no impact on the slope of the calibration curve for o-xylene. Yet, the linear range decreased by 75% to 0-25 mg/L (orange dotted line in Figure 3.6a and Figure A3.7) with minimum observed concentration of 100 µg/L and an R² of 0.9963 when salts were present. The simulated OSTP pore water similarly decreased the linear range by 50% for 1-MN to 0-5 mg/L, with a minimum observed concentration of 100 µg/L and an R² of 0.9906, at a given salt concentration (Figure 3.6b). The data beyond that linear range plateaued and can be seen for o-xylene and 1-MN in Figure A3.13. These minimum observed concentrations in the 20% HPLC MeOH simulated OSTP pore water solution were similar to those observed without salts in the 20% HPLC MeOH simulated OSTP pore water solution and were better than those observed in 20% HPLC MeOH solution with bitumen contamination. Furthermore, the sensitivity between o-xylene and 1-MN signals was not noticeably affected by the simulated OSTP pore water.

Saline solutions have been known to impact the fluorescence signals of various compounds by increasing or decreasing emission spectra. A certain salt ion could have different effects on different fluorophores. For example, quinine bisulphate and uranine fluorescence emissions in aqueous solutions were significantly reduced in the presence of iodide, thiocyanate, bromide, and chlorides (Li, Na, K, Rb and La), (Jette & West 1928). However, increasing Na⁺ salts have increased fluorescence emission responses from dissolved organic carbon in freshwater and estuary samples and a fungal toxin ochratoxin A (Sharma 2018; Esteves et al. 1999). Furthermore, with increased Ca²⁺ concentrations in solution, the fluorescence strength of a fluorescence probe increased at lower excitation wavelengths (<425 nm) and
decreased at higher wavelengths ~425-520 nm; this occurred because Ca\(^{2+}\) bound to the probe (Iatridou et al. 1984). Hence it is reasonable that simulated OSTP pore water (primarily Na\(^+\) salts) could diminish the fluorescence response of one naphtha surrogate (1-MN) yet have a minimal impact on another (o-xylene).

![Figure 3.6: Calibration curves of (a) o-xylene and (b) 1-MN in 3 solutions: RO water, RO water with 20% HPLC grade MeOH, and a simulated OSTP pore water (composition listed in section 3.2.6) with 20 vol.% HPLC grade MeOH which was added for stability.](image)

It is common for ions to form complexes with aromatics in solution that quench fluorescence by providing non-radiative pathways to return from an excited state (Lakowicz 2006). Other mechanisms that quench fluorescence due to the presence of ions exist (e.g., short-range Dexter exchange interactions) however these are quite uncommon (Salthammer et al. 1990; Birch et al. 1993; Lakowicz 2006). Saline structures and molecular interactions between salts and fluorophores have been shown to potentially increase fluorescent signals in a variety of applications, however these molecules are quite different from the aromatics of interest (Lakowicz 2006; Selvam & Sarkar 2017; Villa et al. 2022). Since there are multiple and complex mechanisms by which salts can affect fluorescence, their impact can vary. This investigation of these mechanisms is outside the scope of this thesis yet could prove to be an interesting topic of future research.

51
3.3.8 Analysis of Surrogates in MFT

Although the primary motivation of this research is to understand the partitioning of naphtha surrogates between bituminous and aqueous phases in the OSTPs, there is interest in using fluorescence to measure naphtha components in the aqueous phase of MFT. To investigate the effects of MFT on naphtha surrogate analysis, one volume of an MFT sample was mixed with four volumes of RO water or four volumes of RO water containing 20% HPLC grade MeOH. Samples included samples spiked to 20,000 mg/L of o-xylene and negative controls with no surrogates. 20,000 mg/L was used as o-xylene is expected to strongly partition into the bitumen and MFT solids, and it is the concentration planned for the naphtha mass transfer experiments from bitumen to aqueous phases (Chapter 4). Samples were centrifuged, and the aqueous supernatant was recovered for analysis. Another RO water or 20% MeOH phase was added, and the centrifugation/extraction process was repeated for a total of five times.

While only the data for Pool A – 5 m MFT samples are shown (Figure 3.7), these trends are representative of all MFT samples tested (Figure A3.8 – Figure A3.12). With RO water alone, the amount of o-xylene extracted decreased with each extraction (Figure 3.7a). However, with 20% MeOH, each extraction removed approximately the same amount of o-xylene (Figure 3.7b). The losses from the RO water were not observed with 20% MeOH as o-xylene can be volatilized without a co-solvent and/or preferentially partition into the bitumen in MFT.

From the five aqueous extractions, a maximum of only 4.1% of the o-xylene spiked into the MFT was recovered, with the remaining o-xylene likely still associated with the bitumen in the MFT solids. This indicates that the use of fluorescence spectroscopy to monitor naphtha in MFT needs to be further modified to selectively recover the naphtha and/or bitumen components via partitioning into selective NAPL phases of different hydrophobicities. Total solubilization of all naphtha and bitumen components may result in fluorescence spectra that may be too noisy to be useful.
Figure 3.7: 1-ring aromatic concentration as a function of the number of extractions with fresh RO water or 20% MeOH in RO water of Pond A – 5 m MFT samples with and without 20,000 mg/L spikes of o-xylene which is labelled as “+ Spike”. Plots show the concentration of each extraction (a) using RO water, and (b) using 20% HPLC grade MeOH, and the cumulative concentrations extracted (c) using RO water and (d) using 20% HPLC grade MeOH. For all samples n=3, values are the mean while the error bars are one standard deviation.

As only a small portion of o-xylene was recovered after five extractions (0.14 – 4.13%), obtaining a total amount in the sample is not feasible. However, with the consistency of the extraction concentrations in 20% MeOH (Figure 3.7b and c), it was possible to obtain a reasonable partition coefficient for specific samples, and values were different with different MFT samples (see Figure A3.8 – Figure A3.12).

Unfortunately, with the large number of components in naphtha and the limited number that fluoresce, acquiring individual partition coefficients for all naphtha constituents is not feasible, leaving the use of surrogates to represent naphtha as a reasonable option. It should also be noted that the small portion of o-
xylene extracted (especially with RO water) may be indicative of mass transfer limitations in which the naphtha components are trapped within the bitumen associated with MFT.

To “close” the mass balance, the remaining solids after the five centrifugations were analyzed to determine the total organic carbon content (Table 3.1). While the extractions were performed in triplicate, the total organic carbon measurement required a minimum mass; hence, the triplicate samples were pooled, and the dried mass weighed as $1.89 \pm 0.32$ g.

For the Pond A – 5 m samples, the total organic carbon of the residual MFT solids was similar with and without the o-xylene indicating significant bitumen content, yet there was more organic carbon content than found in Pond B – 12.5 m, and Pond A – 15 m samples. This may indicate a greater extent of degradation in the MFT of the OSTPs as a function of depth or a stronger preferential partitioning to the solids/bitumen in Pond A – 5 m MFT than other MFT samples (Holowenko et al. 2001). However, it should be noted that light non-aqueous phase liquid (LNAPL) phases were observed in Pond B – 12.5 m samples while care was taken to remove them from the analytical phase.

This shows that the partitioning of naphtha constituents between aqueous and bituminous/solids phases in the MFT varies greatly from sample to sample (both between ponds and with pond depth) and between RO water and 20% MeOH usage (Holowenko et al. 2001).

Table 3.1: Total organic carbon (%) of MFT solids after five extractions with RO water or 20% MeOH with and without additional o-xylene spike.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Organic Carbon (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RO Water</td>
<td>20% MeOH</td>
<td>20% MeOH Rinses with Spike</td>
</tr>
<tr>
<td>Pond A – 5m</td>
<td>23.7</td>
<td>25.7</td>
<td>22.2</td>
</tr>
<tr>
<td>Pond A – 15m</td>
<td>24.5</td>
<td>9.6</td>
<td>10.8</td>
</tr>
<tr>
<td>Pond B – 12.5m</td>
<td>16.6</td>
<td>14.1</td>
<td>7.6</td>
</tr>
<tr>
<td>Blank</td>
<td></td>
<td>&lt;0.5</td>
<td></td>
</tr>
</tbody>
</table>

Due to the complexity and breadth of MFT sample compositions, fluorescence analysis is difficult. It can only provide limited insight into the naphtha concentrations in an MFT sample by only analyzing the aqueous phase and due to naphtha’s strong association with bitumen. The composition and variety of MFT samples make analysis difficult. Hence the fluorescence spectroscopy method must be modified further to
track naphtha in MFT. This could be done by simplifying the system to include select NAPL or solid constituents of MFT that most impact naphtha surrogate partitioning. This may aid analysis by decreasing noise in the fluorescence response. Another possible solution is to perform extractions with a third non-aqueous phase. This phase would have to be strongly yet selectively have desired naphtha and bituminous components partition into it and be a chemical such that fluorescence spectroscopy is possible, and very little signal noise occurs.

3.4 Conclusions

Analyzing naphtha and/or naphtha surrogates in an aqueous solution can be expensive (up to $200 per sample) and a long process (>1 hr/sample). A method was required to study the partitioning behaviour of naphtha between bituminous and aqueous phases in the context of Athabascan OSTP MFT. A major benefit of fluorescence spectroscopy is its ease and speed of analysis (requiring ~1 hr for preparation and ~1 min per sample). In this work, a single wavelength excitation, ranged emission scan fluorescence spectroscopy method was developed. It analyzes the aqueous concentrations of naphtha surrogates (o-xylene and 1-MN) using a PTI QuantaMaster 400 spectrometer with a 75-w xenon arc lamp, excitation and emission monochromators, a photomultiplier detector and PTI FelixGX Software. In this method the use of MeOH as a co-solvent to aqueous samples, naphtha surrogates (o-xylene and 1-MN), bituminous contamination without MFT enabled detection of changes on the scale of ~1 ppm as opposed to the scale of ~1,000 ppm of naphtha when using SPME with ethanol and MFT samples (Moe 2021). Hence, this method was sufficient for its desired applications.

The lighter monoaromatic naphtha surrogate, o-xylene, was selected since toluene can be “analytically dirty”. O-xylene also had a slightly larger linear range and better linear response than toluene. For the heavier di- and tri-aromatics, 1-MN was chosen over anthracene, as 1-MN emitted a more symmetric fluorescence spectrum as opposed to anthracene which emitted spectra with multiple peaks. A single steady-state excitation at 260 nm and emission scans at 270-410 nm was used to quantify o-xylene and 1-MN, respectively, by integrating the emission response ranges of 270-300 nm and 315-410 nm.
The use of MeOH as a co-solvent (20 vol%) and sample handling techniques to minimize exposure to open air reduced the volatilization of o-xylene and 1-MN in stored samples, resulting in more consistent fluorescence signals. Samples should be measured within 6 days of preparation.

The fluorescence spectra of water-soluble bituminous compounds and the naphtha surrogates had some overlap, resulting in some variance in the linearity and minimum observed concentration in the calibration curves of o-xylene and 1-MN. Increasing contact time between the aqueous phase and a bitumen droplet resulted in increased concentrations of water-soluble bituminous compounds, which negatively affected linearity and minimum observed concentrations. However, the linearity and detection limits were reasonable if their fluorescence signals were corrected with naphtha-negative, bituminous-positive aqueous controls, which were in contact with bitumen for the same length of time as the test sample. The minimum observed concentration ranged from 100 µg/L - 1 mg/L for o-xylene and 10 – 100 µg/L for 1-MN, while the highest concentrations in the linear range were 30-100 mg/L and 5-10 mg/L for o-xylene and 1-MN, respectively.

The potential for interference between the two naphtha surrogates was investigated. This method was developed for a ~10:1 ratio of o-xylene:1-MN, where interference did not significantly impact the performance of fluorescence spectroscopy. However, interference at other ratios (e.g., 1:1 or 100:1) could impact analysis but can still be used if calibration curves are generated at the appropriate ratios.

Simulated OSTP pore water decreased the slope of the fluorescence response for 1-MN and decreased the linear range by 50% to 0-5 mg/L. For o-xylene, the slope of the fluorescence response was not impacted, but the linear range decreased by 75% to 0-25 mg/L. The minimum observed concentration for both surrogates was 100 µg/L. Hence a new calibration curve using simulated OSTP pore water is needed.

Finally, the fluorescence spectroscopy method was tested on repeated extractions of MFT samples with RO water and 20% HPLC MeOH. Only 4.1% of o-xylene added was recovered in the aqueous phase from five extractions of the “solids” of MFT (bitumen, sands, silts, and clays). Partition coefficients can be
determined for naphtha surrogates between the “solids” of MFT and the aqueous phase. Using select naphtha/bituminous components that can partition between an aqueous phase and a less complex NAPL phase could improve the repeatability and quantification of the partitioning.

3.5 References


Whitley, Paula, and Mesha Thompson. 2022. “Queen’s University Analytical Services Unit Work.” *Personal Communication*.
Chapter 4

Mass Transfer of Naphtha Between Bitumen and Aqueous Phase

Abstract

Greenhouse gas emissions from the Athabascan Oil Sands Tailings Ponds (OSTPs) cause environmental concern with their rates, composition of CO$_2$ and CH$_4$ as a consequence of the biodegradation of naphtha diluent. The bio-genic mechanisms of this degradation are well understood. However, experiments performed with MFT have had unexpected results, indicating limitations to CO$_2$ and CH$_4$ production rates. The bio-accessibility of naphtha solubilized within the bituminous phase is a likely cause.

To study the mass transfer effects of naphtha solubilized in bitumen a process was developed to recover bitumen from bitumen froth to ensure experimental homogeneity and consistency. The bitumen was spiked with naphtha surrogates (i.e., o-xylene and 1-MN), and droplets were placed at the bottom of vials filled with an aqueous phase. The surrogates diffused from the sessile bitumen droplets into the aqueous phases, which were sacrificially recovered and analyzed after 30 min to 100 d. The initial concentration of surrogates in the bitumen had minimal observed effect on mass transfer rates into the aqueous phase. These rates varied considerably between o-xylene and 1-MN and between RO water and simulated OSTP pore water. For ~1 cm diameter bitumen droplets ($120 \leq \eta \leq 870$ Pa s), mass transfer was poorly characterized by one lumped mass transfer coefficient ($\lambda$) compared to two, a larger $\lambda$ represented faster dissolution over the first 7-14 d, and the second represented subsequent slower transfer. This occurred with initially homogenous bitumen droplets and reactors which had their aqueous phase replaced after an apparent equilibrium was reached. Not only did rates, but the mass transfer properties changed over time. This could be caused concentration gradients within the bitumen droplet, depleting the surrogates at the bitumen-aqueous interface relative to the bulk bitumen, consequently limiting their dissolution into the aqueous phase. Further research is required to investigate and quantify the effects of interfacial film formation and/or intra-bitumen diffusional limitations.
4.1 Introduction

Canada’s Athabascan oil sands are one of the world's largest petroleum reserves, covering 142,200 km² and accounting for ~39% of Canada’s total oil production (Small et al. 2015; Oil Sands Discovery Center (OSDC) 2023). Approximately half of the bitumen production in the region was generated from open-pit mining in 2021 (Alberta Energy Regulators (AER) 2023). The Clark’s hot water extraction process (CHWEP) recovers bitumen from open pit mined ores using hot water, NaOH, a diluent (naphtha based or paraffinic) and aeration (Rao & Liu 2013). This process generates solid aqueous waste of 0.5-5.0 wt.% bitumen with up to 30% of the (naphtha) diluent solubilized within (Burkus et al. 2014; Afara et al. 2010). This waste is stored in the oil sands tailings ponds (OSTPs) (Penner & Foght 2010; Chalaturnyk, et al. 2002). However, significant greenhouse gas (GHG) emissions are observed from these ponds many years after an OSTP is first used (~15 years in the case of Syncrude's Mildred Lake Settling Basin was first used) (Guo 2009). As GHG-induced climate change is a significant world problem, this is a topic of concern.

The solids and bituminous waste settle over the years and, with depth, excreting interstitial water and increasing the density in the ponds' deeper layers: fluid fine tailings (FFT) and mature fine tailings (MFT). MFT is the deepest and most dense at ≥ 30 wt./vol.% solids and generally occurs after 5-10 years of settling. Methanogenic conditions exist in FFT and MFT where microbial activity degrades naphtha, generating GHGs that can diffuse into the atmosphere. Overall, an estimated 33,100 tons of CH₄ and 423,000 tons of CO₂ are emitted annually every year from Suncor’s, Syncrude’s, and Shell Albian’s ponds in the Athabasca region which accounts for 0.65% of the industries GHG emissions in the oil sands sector in Alberta (Foght et al. 2017; Baray et al. 2018; Oil Sands Discovery Center (OSDC), 2023). This work is focused on the MFT several meters deep in OSTPs that are producing GHG emissions after several decades of use.

Methane has a global warming potential 27-30 times greater than CO₂ over 100 years as of July 31st 2023 (US EPA 2023). In 2015, the Government of Alberta announced that methane emissions must be reduced by 45% of the 2014 levels by 2025 (AER 2023b). The major source of biogenic methane in these
The naphtha diluent is a mixture of primarily C5-10 hydrocarbons, composed of ~7% cyclohexanes, ~15% cyclopentanes, ~31% larger compounds of unconfirmed composition (e.g., naphthalenes), and the remaining are small non-cyclic alkanes (Speight 2019). To aid in analyzing naphtha experiments, surrogate chemicals that represent specific groups of naphtha constituents can be used instead (Shafieiyoun & Thomson 2018). There is significant research into the biodegradation of naphtha in OSTPs, notably showing limitations to biodegradation, such as poor bio-accessibility of naphtha (Siddique et al. 2006; Siddique et al. 2007; 2008; Ramsay et al. 2021). In addition, naphtha bioavailability can be limited by its mass transfer from the bituminous to aqueous phases. These rates can be affected by the viscosity and geometry of bitumen droplets and their aqueous interface (Nelson et al. 1996; Shafieiyoun & Thomson 2018; Endo et al. 2012). Furthermore, varying salinity within and between ponds can decrease naphtha concentrations through the "salting-out" effect where increasing salts concentrations breaks up the structure of the water reducing the aqueous solubility of naphtha (Nelson et al. 1996; Shafieiyoun & Thomson 2018; Endo et al. 2012).

Experiments with coal tar from former manufacturing gas plants at the bottom of a water column fit a multicomponent-multiphase model for organic compounds diffusing from dense non-aqueous phase liquid (DNAPL) to aqueous phases (Shafieiyoun & Thomson 2018). Similar experiments are performed in the present work on naphtha diffusion from bituminous to aqueous phases to provide more context on naphtha degradation and GHG generation rates in OSTPs.

In this work, three studies were performed - (1) evaluation of the mass transfer of naphtha within a bitumen droplet, i.e., on the NAPL (bituminous) side of the interface, (2) determination of the effect of aqueous salts and naphtha surrogates on mass transfer rates, and (3) investigation of the potential for interfacial film formation and its possible impact on bituminous to aqueous mass transfer.
4.2 Material and Methods

4.2.1 Separation of Bitumen from Bitumen Froth

Bitumen froth was received in a 10-gal drum. The drum was placed on a Drive Roll mixer (2 rollers x 2” in diameter x 2’ long, Sepor Inc.) for 3 h at 30 rpm before 0.5-1 L samples were taken. Bitumen froth was added to reverse osmosis (RO) water at a 1:3 volumetric ratio in 150 mL Pyrex centrifuge tubes, tightly capped, then heated to 95°C in a water bath before centrifuging at 8,000 rpm for 20 min using a Sorvall RC-5B centrifuge. Of the four phases obtained, the light non-aqueous phase liquid (LNAPL) and aqueous phases were individually removed by pipetting. Then the tube was heated to 75 °C to allow the bitumen to be pipetted from the top of the solids.

Figure 4.1: (Left) photo of centrifuge tubes containing bitumen froth after centrifugation with reverse osmosis water. Aqueous and LNAPL phases cannot be seen due to a thin layer of bitumen coating inside the tubes. (Right), a cross-sectional schematic illustrating the relative amount of solids, bitumen, aqueous and light non-aqueous (LNAPL) phases.

4.2.2 Bitumen Characterization

The viscosity of bitumen spiked with 0, 1, 2, or 4 wt.% o-xylene and 1-MN and of bitumen alone was analyzed using a REOLOGICA Instruments AB rotational viscometer with a 1 mm gap to a 25 mm radius ETC plate. After sample trimming, the heater casing was closed around the plate and set to 20, 30, or 40°C for 120 s. Once the loading force dropped below $4.074 \times 10^4$ Pa or after 300 s (whichever came first), the
gap was set to 1.005 mm for a final sample trimming. After trimming, the gap was reset to 1 mm, the heater casing re-closed, and after 30 s to establish temperature equilibrium, the rotor was released, and increasing shear was applied until deformation of the bitumen occurred (i.e., a steep decrease in viscosity as a function of shear rate).

About 40 mL of bitumen was added to a graduated cylinder (sensitive to 0.1 mL) and pre-weighed to four decimal places using a Sartorius Cubis Balance. The cylinder was covered and undisturbed for 4 h to allow cooling and time for the viscous bitumen to settle.

4.2.3 Spiking Bitumen with Naphtha Surrogates

About 20 g of bitumen was pipetted into scintillation vials with an appropriate mass of o-xylene and 1-methylnaphthalene (1-MN) before the vials were tightly covered with Teflon-lined caps. The vials were heated to 80-85°C in a water bath for 30 min then vortexed for 5 min. These conditions were chosen as it was the highest temperature in which there were no significant losses and allowed handling of the bitumen.

4.2.4 Simulated Oil Sands Tailings Pond Pore Water

Simulated oil sands tailings pond (OSTP) pore water was made by averaging the major salts in the pore water of three samples from two OSTPs in the Athabascan region, Pond A or PA (samples taken at depths of 5 m, and 15 m), and Pond B or PB (with samples taken a depth of at 12.5 m). The composition used was 0.025 mg/L NH₄Cl, 0.5484 mg/L NaCl, 0.5220 mg/L Na₂SO₄, and 1.3082 mg/L NaHCO₃ and had a similar conductivity (~4,200 µs/cm) to the pond samples (Gee et al. 2017).

4.2.5 Mass Transfer Experiments

4.2.5.1 Diffusional Mass Transfer in Static Bitumen Drop Equilibration

Spiked bitumen containing 0, 2, or 4 wt.% of o-xylene and the same mass of 1-MN was heated to 75 - 80 °C in a water bath immediately after it was prepared to decrease the viscosity to permit pipetting 0.5 ± 0.2 g of the spiked mixture into the bottom of 24 mL glass scintillation vials before tightly sealing with Teflon-
lined caps. Once cooled to room temperature, RO water or simulated OSTP pore water was gently pipetted along the side of the vial to fill the headspace above the bitumen drop. The bitumen stays at the bottom of the scintillation vial with a diameter of 1 cm. Hence it was assumed that bitumen is completely flat with a surface area of ~3.14 cm² and the 23 mL aqueous control volume existed as a column directly above the bitumen. The reactors were stored in static, dark conditions. The experiment was performed in triplicate, and vials were sacrificially sampled over 70 d. To sample a sacrificed vial, the aqueous phase (~21 mL) was gently pipetted without disturbing the bitumen into a clean scintillation vial already containing 4 mL of high-performance liquid chromatography (HPLC) grade MeOH (an additional ~1 mL of MeOH was then added to achieve a final 20 vol.% solution) and analyzed by fluorescence spectrophotometry.

Figure 4.2: Schematic of the experimental setups where the black shapes represent the bitumen droplets in an aqueous phase while the yellow arrows indicate the direction of mass transfer or vortexing/agitation. (Left) is the sessile diffusional experiment. (Right) depicts an agitation-forced equilibrium experiment.

4.2.5.2 Forced Equilibrium Experiments

In forced equilibrium experiments, 0.5 ± 0.2 g of bitumen spiked with 0, 1, 2, 3, or 4 wt.% o-xylene and 1-MN was pipetted into the bottom of 24 mL glass scintillation vials, sealed with a Teflon-lined cap then placed in an 80°C water bath for 30 min, and vortexed for 5 min. The vial’s contents were an aqueous phase and a homogenous black liquid, which later settled into many (~1 mm diameter) bitumen drops suspended in the aqueous phase. After 7-10 d under dark, static conditions, all the visible bitumen had settled. Next,
the aqueous phase was gently pipetted into a clean vial containing 4 mL of HPLC grade MeOH and then analyzed via fluorescence. This experiment was independently repeated four times under the same conditions as the sessile diffusional experiments.

4.2.5.3 Aqueous Phase Flushing

The aqueous phase flushing experiments used the same triplicate reactor setup as the static bitumen droplet and the forced equilibration experiments. After the vials were stored in static, dark conditions for 150 d (RO water) or 73 d (simulated OSTP pore water), the entire aqueous phase was pipetted off, carefully replaced with the RO or simulated OSTP pore water (the same type of aqueous phase as was removed) without disturbing the bitumen, and further stored for 30 min to 53 d. Finally, the replenished aqueous phase was sacrificially sampled and analyzed via fluorescence spectroscopy.

Table 4.1: Summary of the four conditions tested independently in the diffusional mass transfer experiments.

<table>
<thead>
<tr>
<th>Aqueous Phase</th>
<th>O-xylene and 1-MN Spikes in Bitumen Drop (wt.%)</th>
<th>Description at “t=0”</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO water</td>
<td>0, 2, and 4</td>
<td>Initially homogenous bitumen droplet</td>
</tr>
<tr>
<td>Simulated OSTP pore water</td>
<td>0, and 4</td>
<td>Replaced aqueous phase after apparent equilibrium was reached (~150 d)</td>
</tr>
<tr>
<td>RO water</td>
<td>0, 2, and 4</td>
<td>Replacement of the aqueous phase after apparent equilibrium (~73 d)</td>
</tr>
<tr>
<td>Simulated OSTP pore water</td>
<td>0, or 4</td>
<td></td>
</tr>
</tbody>
</table>

4.2.6 Fluorescence Spectroscopy

Aqueous samples in 20% methanol were vortexed for 30 s, and 3 mL was pipetted into a 1 cm quartz cuvette, covered, and wiped clean with a Kimwipe before insertion into a PTI QuantaMaster 400 spectrometer equipped with a 75 W xenon arc lamp, excitation and emission monochromators and a photomultiplier detector. The lamp temperature was allowed at least 30 min to stabilize, then using 6 nm slits, fluorescence responses were measured at 1 nm increments with a 0.3 s integration time using PTI FelixGX Software. Samples were excited at 260 nm, and emissions were measured at 270-410 nm, where the 270-300 nm and 315-410 nm emissions were integrated to determine the o-xylene and 1-MN
concentrations, respectively. A calibration curve of o-xylene and 1-MN in 20% HPLC grade MeOH was prepared using 20% HPLC grade MeOH in RO water as a blank. Two rinses with RO water and MeOH of the cuvette were done between samples. It should be noted that this method does not distinguish between o-xylene and different one-ring, or between 1-MN and different two-ringed aromatics.

4.3 Results and Discussion

4.3.1 Bitumen and Naphtha Surrogate Mixture Density and Viscosity Determination

The viscosities of bitumen spiked with 0, 1, 2, or 4 wt.% o-xylene and 1-MN and of bitumen alone were measured at near zero shear at 20, 30, and 40 °C (section Bitumen). Viscosity decreased as a function of temperature and mass fraction of o-xylene, and 1-MN solubilized. Triplicate samples were combined and then analyzed. This was repeated for 0 and 1 wt.% spikes at 20 and 40°C, respectively (Table A4.2).

Approximately 40 mL of bitumen was measured in pre-weighed graduated cylinders and weighed (4.2.2). The samples were left to cool undisturbed for 4 h to ensure accurate volume measurements. With triplicate samples, the densities were 1.0875 ± 0.014 g/cm³.

4.3.2 System Equilibria

4.3.2.1 Forced Equilibria

0 wt.% spike (or only bitumen) trials showed aqueous o-xylene and 1-MN concentrations (“background signals”) of 5.7 ± 2.3 mg/L and 0.9 ± 0.2 mg/L, respectively, in RO water and 6.5 ± 0.4 mg/L and 0.9 ± 0.04 mg/L in simulated OSTP pore water. These background signals were subtracted from the spiked trial signals to determine the contributions from the naphtha surrogates.

Experiments showed a linear increase of o-xylene and 1-MN aqueous solubility, correlated to the initial mole fraction in bitumen (which was determined using an assumed 700 molecular weight of bitumen (Champagne et al. 1985)) with an R² of 0.965 and 0.966 for o-xylene and 1-MN, respectively, in RO water and 0.940 and 0.920 in simulated OSTP pore water (Figure 4.3). For all trials, the residuals were not randomly distributed, for the simulated OSTP pore water trials there were approximate zero value residuals.
then negative and then positive residuals with respect to mole fraction. For the RO water trials the concentrations appear to potentially plateau at higher mole fractions (Figure A4.1). Hence these relationships may lose linearity at higher mole fractions. However, this study only uses mass fractions of 0-4 wt.%; hence these relations are sufficient for this work. RO water the 1-MN regression yielded larger residuals than o-xylene with an apparent plateau at mole fractions higher than 0.08 (Figure 4.3b).

![Figure 4.3: Forced equilibrium concentrations of o-xylene and 1-MN partitioning from bitumen into RO or simulated OSTP pore water as a function of their initial mole fraction within the bitumen droplet which was determined using an assumed 700 molecular weight of bitumen (Champagne et al. 1985). For all samples (n=3), and error bars are one standard deviation.](image)

For any initial mole fraction (acquired from wt.% and assuming a 700 molecular weight of bitumen (Champagne et al. 1985)) in a bitumen droplet, the effective solubility in simulated OSTP pore water was ~half of that with RO water (154 ± 20 vs. 299 ± 29 mg/L/(mol_o-xylene/mol_bitumen+surrogates) and 15 ± 2.2 vs. 37 ± 3.7 mg/L/(mol_1-MN/mol_bitumen+surrogates)) demonstrating that salt addition decreased the equilibrium concentration of 1-MN.

4.3.2.2 Thermodynamic Equilibrium Fugacity Modeling

The single simulated OSTP pore water solution does not represent the full range of the pore water found in OSTPs. Hence, other solutions were studied using a model developed by Dr. Stephen Brown,
Environmental Sciences and Chemistry at Queen’s research group, which combines theoretical thermodynamic principles with empirical correlations (Moe 2021). Experimental partition coefficients were determined for organic compounds between water and polydimethylsiloxane polymer rods and between water and bitumen (Moe 2021). Combined with theory (A4.1), these correlations were used to generate a model and predict o-xylene and 1-MN concentrations in RO water and saline solutions (Figure 4.4).

Model o-xylene concentration predictions in RO water were consistently lower than forced equilibrium experiments (by 14.1 ± 1.9 mg/L). Slopes of the aqueous concentrations as a function of the initial mole fraction in bitumen are similar at higher concentrations, 5.85 ± 0.38 and 7.451 ± 0.001 mg/L/mol\textsubscript{o-xylene}/mol\textsubscript{bitumen+surrogates} for the model and experiments, respectively (Figure 4.4a). However, the model was poorly fit for experimental data ($R^2 = 0.21$). O-xylene predictions were better for simulated OSTP pore water with slopes of 7.187 ± 0.001 and 7.5 ± 0.8 001 mg/L/mol\textsubscript{o-xylene}/mol\textsubscript{bitumen+surrogates}, an average value difference of 4.4 ± 0.9 mg/L, and $R^2$ value of 0.87 (Figure 4.4c).

Predictions for 1-MN in RO water (Figure 4.4b) agree with experimental concentrations with an average difference of 0.65 ± 0.53 mg/L, slopes of 1.345 ± 1x10$^{-16}$ and 1.19 ± .29 mg/L/mol\textsubscript{1-MN}/mol\textsubscript{bitumen+surrogates} respectively and an $R^2$ value of 0.83. However, predictions for 1-MN in simulated OSTP were inaccurate, with an average difference of 1.9 ± 0.6 mg/L and an $R^2$ of -2.7 (Figure 4.4d).

Seawater was also modelled to represent a maximum salinity or lowest solubility scenario with an ionic strength of 0.704 mol/L vs. 0.0676 mol/L for simulated OSTP pore water (Pierfelice 2013). Fitting the seawater model to the simulated OSTP pore water results yielded $R^2$ values of 0.63 and 0.81 for o-xylene and 1-MN, respectively. The seawater model yields similar to better performance than fitting the appropriate simulated OSTP pore water model indicating the model is not helpful for predictions for a wide range of salinities (Figure 4.4c-d).

A major drawback of these experiments and the interpretation of their results is that non-fluorescent residual naphtha and/or bitumen components can solubilize into the aqueous phase and may not have been
measured in the background signals (section Chapter 3). This possibility was not considered in the thermodynamic fugacity equilibria model but could reduce the effective solubility of o-xylene and 1-MN.

![Graphs showing equilibrium concentrations for different scenarios](image)

**Figure 4.4:** Aqueous phase concentrations as a function of the initial mole fraction of naphtha surrogate in the bituminous phase with an assumed 700 molecular weight of bitumen (Champagne et al. 1985). The experimental equilibrium and the theoretical fugacity-based model predictions are compared for (a) o-xylene, and (b) 1-MN in RO water, and (c) o-xylene, and (d) 1-MN in simulated OSTP pore water with fugacity model predictions for seawater as a maximum saline scenario. For all experimental samples (n=3), and error bars are one standard deviation. For the models error bars are sensitivity based on model parameters.

### 4.3.3 Sessile Diffusional Experiments

The primary focus of this work is to understand the mass transfer rate of naphtha surrogates from the bituminous to aqueous phases in OSTPs. Knowing the equilibrium concentration of a system greatly
improves the ability to study mass transfer phenomena. While fugacity modelling for some data sets indicates that equilibrium concentrations were reached in the forced equilibrium experiments, this was not the case for all experimental data. Consequently, the model should not be used as the sole predictor of equilibrium concentrations. Hence, the diffusional mass transfer experimental reactors studied had the same overall compositions as the forced equilibrium experiments (section 4.3.2.1).

4.3.3.1 Initial Homogenous Bitumen Droplet

Vials (in triplicate) with initially homogenous bitumen droplets of 0 (background trials), 2 or 4 wt.% o-xylene and 1-MN) were in sessile contact with an aqueous phase (RO or simulated OSTP pore water) which was sacrificially sampled after 0.5 to 61 d. To determine the contributions of the spiked surrogates, the background trials investigated residual one-ring and two-ring aromatic signals from bitumen. The background bituminous signals did not statistically increase over the duration of the experiment, with p-values for significant slope existence of 0.638, 0.514, 0.214 and 0.221 for RO water and 0.0503 and 0.0013 for simulated OSTP pore water (compared to $\alpha=0.05$). Hence the background signals were averaged and subtracted from the 2 wt.% (RO water only) and 4 wt.% trials to determine the contributions of additional o-xylene and 1-MN to the spiked signals (Figure 4.5).
Figure 4.5: Aqueous concentrations of naphtha surrogates in sessile bitumen droplet diffusion experiments of (a) o-xylene, and in (b) 1-MN in RO water and, (c) o-xylene, and (d) 1-MN in simulated OSTP pore water. Background signals were subtracted from the 2% and 4% concentrations from those with naphtha surrogates initially solubilized in the bitumen. The dotted lines indicate results from the forced equilibrium experiments (section 4.3.2.1). All reactors were sampled sacrificially (n=3), and error bars are one standard deviation.

When the observed concentrations in a trial plateaued and did not change for three or more weeks, it was deemed as an “apparent equilibria”. While there is no certainty that this is the true experimental equilibrium, it was sufficient for this work. The equilibria values were obtained by taking the mean of the final concentrations that did not differ from each other. The “apparent equilibria” achieved after ~7-10 d for the 2 and 4 wt.% RO water experiments were not statistically different from each other with the smallest t-test p-values of 0.13 and 0.38 for o-xylene and 1-MN, respectively, compared to α=0.05 (Table A4.3). This was not expected as doubling the naphtha concentration in the bitumen should result in increased
equilibrium concentrations if the aqueous phase is not saturated (as indicated by the forced equilibrium experiments in section 4.3.2.1). This could possibly indicate that the true equilibria concentrations were not reached in the sessile droplet diffusional experiments. The “apparent equilibria” were statistically similar to forced equilibrium concentrations for 2 wt.% o-xylene and 4 wt.% 1-MN in RO water with 33.1 ± 3.1 mg/L vs. 36.2 ± 3.9 mg/L and 6.1 ± 1.2 mg/L vs. 4.5 ± 0.7 mg/L respectively. However, all other trials varied from forced equilibria experiments, with 4 wt.% o-xylene and 2 wt.% 1-MN in RO water varying from 5.8 ± 0.4 mg/L vs. 4.1 ± 0.4 mg/L and 37.3 ± 4.2 mg/L vs. 47.8 ± 3.2 mg/L (Table A4.3), while the 4 wt.% simulated OSTP pore water trials were much lower with 34.4 ± 3.2 mg/L vs. 17.5 ± 2.2 mg/L and 2.6 ± 0.7 mg/L vs. 1.1 ± 0.1 mg/L for o-xylene and 1-MN respectively (Table A4.3).

The “apparent equilibria” in RO water being higher than the forced equilibria for 1-MN and similar for o-xylene could be due to solubilized bituminous compounds. The agitation of the forced equilibria experiments may have solubilized non-fluorescent bituminous compounds to higher aqueous concentrations than would exist at equilibrium in a sessile diffusional experiment. If this occurred, it is possible that those higher concentration compounds were more soluble than 1-MN, effectively occupying the aqueous phase and limiting the amount of 1-MN which can be solubilized.

For all trials, the error bars for the concentrations are quite large, and is likely due to contributions of bitumen to the o-xylene and 1-MN signals. As bitumen is difficult to handle, bitumen droplets were not always the same size (i.e., 0.5 ± 0.2 g) which could lead to varying contributions. Furthermore, non-homogeneity of the initial bitumen droplets could contribute to the large variation. All bitumen and vials were prepared in batches for each trial and were selected randomly for sacrificial sampling to mitigate the effects of these issues on the overall trends, but it did not eliminate deviations between individual samples.

The difference in the simulated OSTP pore water may have been due to the presence of salts where the energy required to dissolve a molecule of o-xylene or 1-MN may have been sufficiently increased at the observed concentration equilibria in the sessile droplet experiments. The mechanical agitation in the forced equilibrium experiments may have provided the energy to overcome this barrier. An interfacial film
may also cause this decrease. In submerged coal tars, the water/coal tar interface undergoes visible film formation, influencing the fluid mass transfer properties of the coal tar (Nelson et al. 1996). These films can have more heavier (e.g., two-ring aromatics) and less light hydrocarbons (e.g., 1-ring aromatics) than the bulk coal tar (Nelson et al. 1996). If such films were present in the sessile droplet diffusion experiments, effectively reducing the o-xylene concentration gradient between the bitumen and aqueous phase, the “apparent” equilibrium concentrations relative to “forced equilibrium” experiments would also be reduced.

The 2 and 4 wt.% RO water trials were similar in both rate and final concentration (Figure 4.5a-b), which was unexpected. This could indicate potential mass transfer limitations on the bitumen side of the interface, as changing the initial “driving force” (concentration gradient) for mass transfer had little impact. Furthermore, additional naphtha surrogates decreased the viscosity (Table A4.2), which should increase homogeneity within the droplet and, consequently, mass transfer rates (if concentration gradients within the bitumen droplet were the cause of this).

### 4.3.3.1.1 Varying Mass Transfer Properties

In this work, bitumen with a diameter of 1 cm sits at the bottom of a scintillation vial. Hence it was assumed that bitumen was completely flat with an effective surface area of ~3.14 cm². A 23 mL aqueous control volume existed as a column directly above the bitumen. If the bitumen and aqueous phases stay separate, yet each is well-mixed with constant properties, the mass transfer of naphtha can be described using a simplified differential equation (4.1).

\[
\frac{\partial C_w}{\partial t} = \lambda_i (C_{eq}^w - C_w) - k_i C_w
\]  

(4.1)

\(C_w\) is the aqueous naphtha concentration, \(C_{eq}^w\) is the aqueous naphtha equilibrium concentration, \(k_i\) is a first-order biodegradation rate of the naphtha in the aqueous phase, and \(\lambda_i\) is a lumped mass transfer coefficient (which combines the effective mass transfer surface area [m²] with a standard mass transfer
coefficient [m/s] for final units of [m³/s]). Assuming abiotic/no bio-degradation conditions, and a constant \( \lambda_i \) the solution to equation (4.1) is described by (4.2) as a function of time.

\[
1 - \frac{C^w}{C_{eq}^w} = p \cdot e^{\lambda_i t}
\]  

(4.2)

However, under non-ideal conditions, the original relation does not hold; hence an arbitrary coefficient (p) for \( \lambda_i \) can be used to describe the behaviour.

In abiotic (no reaction) trials with a well-mixed bitumen droplet and no intra-NAPL mass transfer limitations, this relationship should hold for a single value of \( \lambda_i \) (“p” = 1) over the entire duration of each trial. However, in all trials (except the 4% initial spike of o-xylene in bitumen and simulated tailing pond pore water), the plots of \( 1 - C^w/C_{eq}^w \) vs. t were better described with two distinct lumped mass transfer coefficients (Figure 4.6). It should be noted that these two distinct lumped mass transfer coefficients do not necessarily represent two distinct mass transfer phenomena; rather, it approximates a shift in mass transfer properties over time (whether discrete or continuous).

Figure 4.6: Integrated mass transfer data for the sessile bitumen droplet experiments equation (4.2) of (a) 4 wt.% o-xylene in RO water and (b) 4 wt.% 1-MN in simulated OSTP pore water. These two datasets are representative of all the trials performed (Figure A4.2). All data sets were fitted with a single lumped mass transfer coefficient (\( \lambda_i \)) (equation (4.2)) and two distinct mass transfer coefficients (indicating a change in mass transfer properties over time).
While the regression of the data resulted in some strong correlations when using a single $\lambda_i$ (“p” = 1) value (the 4% o-xylene and 4% 1-MN trials in RO water with $R^2$ values of 0.904 and 0.9721 respectively), there was a large discrepancy between the predicted and experimental values within the first 10 d for all data sets with better agreement occurring around 60 d (as indicated by the residuals in Figure A4.3). This trend was observed for all single $\lambda_i$ models and also for the first parameter (“p” = 1) of the two $\lambda_i$ model ($0 < p \leq 1$) fits (the second of which showed even residual distribution (Table A4.6). This lack of fit indicates that a single lumped mass transfer rate coefficient does not well describe the system.

The two-parameter fits had decreasing $\lambda_i$ values and yielded better predictions for RO water trials ($R^2$ values of 0.9404 and 0.999 compared to 0.13-0.972 for a single-parameter fit) than the simulated OSTP pore water trials ($R^2$ values of 0.253-0.892 and compared to 0.523-0.804 for a single-parameter fit). The two-parameter fit does not represent two distinct and separate conditions, each described by a different parameter. Rather the system’s mass transfer properties would be expected to change continuously. The need for more than one parameter to approximate the behaviour further indicates that the assumption of well-mixed (yet separate) phases does not hold over the entire experiment.

The decreasing $\lambda_i$ values in the two-parameter fit could imply there are mass transfer limitations on the bitumen side of the interface with outer layers of the bitumen droplet (e.g., the bitumen/aqueous interface) becoming depleted of naphtha surrogates and not quickly replenished with naphtha from the center of the droplet due to its high viscosity. It is also possible that an interfacial film between the bitumen and aqueous phases formed (section 4.3.3.1), reducing the concentration of naphtha at the interface with higher concentrations of water and heavier NAPL constituents (Nelson et al. 1996). As this two-parameter fit is an approximation, further work and modelling are still needed to describe these systems better.

4.3.3.2 Aqueous Phase Replacement

As in section Initial Homogenous Bitumen Droplet, bitumen droplets were initially homogenous and were in sessile contact with an aqueous phase in a scintillation vial for 150 d (RO water) or 73 d (simulated OSTP pore water), after which all the aqueous phases were replaced without disturbing the bitumen droplets. The
vials were stored in dark sealed and sessile conditions, and their aqueous phases were sacrificially sampled in triplicate over 0.5 h to 53 d (section 4.2.5.3).

As there was very little o-xylene and 1-MN removed from the aqueous phases in the previous initially homogenous bitumen droplet experiments in section 4.3.3.1 (only 4.1 ± 1.0% and 4.6 ± 0.3%, respectively), the initial mass fractions of o-xylene and 1-MN in the bitumen droplet for this aqueous phase replacement experiment should be similar. In the case of a well-mixed bitumen droplet, it would be expected for little change in the results of the experiments to occur. However, the RO water post-replacement trials took significantly longer than the pre-replacement trials to reach apparent equilibria (Figure 4.7, supporting that the o-xylene and 1-MN were not evenly distributed throughout the bitumen droplet or that an interfacial film had formed (section 4.3.3.1).

0% “background” trials showed no significant concentration slope over time (p-values of 0.135 and 0.0548 for o-xylene and 0.085 and 0.103 for 1-MN compared to α=0.05). Hence the background signals were averaged and subtracted from the 2.0 wt.% spike to determine the contributions of the spiked naphtha surrogates. It was found that for both o-xylene and 1-MN, the post-replacement apparent equilibria were lower than the pre-replacement trials (23.5 ± 2.3 vs. 36.4 ± 3.1 and 1.8 ± 0.5 vs. 6.6 ± 0.4 for o-xylene and 1-MN respectively). Furthermore, the post-replacement trials were lower than the forced equilibria trials (23.5 ± 2.3 vs. 36.2 ± 3.9 and 1.8 ± 0.5 vs. 4.1 ± 0.4 for o-xylene and 1-MN, respectively). All differences were statistically significant (Table A4.5).

~3.93 wt.% o-xylene and ~3.99 wt.% 1-MN were expected to be present and not evenly distributed in the bitumen droplets when the simulated OSTP pore water was replaced (73 d) as only 1.84 ± 0.03% and 0.13 ± 0.03% of the original o-xylene and 1-MN spike were recovered. The background trials showed no significant slope (p-values of 0.267 and 0.197 for o-xylene and 1-MN, respectively, with α=0.05) and were subtracted from the 4 wt.% trials.
Figure 4.7: Aqueous concentrations of the sessile diffusional experiments (pre-replacement) (also shown in Figure 4.5) are overlayed with the concentrations of the aqueous phase replacement experiments (post-replacement) for comparison (time-scale resets to 0 at the time of the aqueous phase replacement). Data are shown for (a) o-xylene pre- and post-replacement in RO water (2 wt.% spikes and background), (b) 1-MN pre- and post-replacement in RO water (2 wt.% spikes and background), (c) o-xylene and 1-MN pre- and post-replacement in simulated OSTP pore water (4 wt.% spikes and background), and (d) zoomed plot of 1-MN pre- and post-replacement in simulated OSTP pore water (4 wt.% spikes and background). The dotted lines represent forced equilibrium results (section 4.3.2.1). For all samples (n=3), and error bars are one standard deviation. Post-flush trials were expected to contain >98% of o-xylene and 1-MN as the pre-flush trials at t=0.

These post-replacement experiments achieved a similar apparent equilibrium concentration to the pre-replacement experiment with p-values of 0.34 and 0.36 (Table A4.5). However, it took longer (21 vs. 10 d) to reach these apparent equilibria for o-xylene, again supporting the theory that non-homogenous bitumen droplets are limiting mass transfer. While for 1-MN, both pre- and post-replacement took ~31 d,
with a lower solubility than o-xylene (28.5 mg/L vs. 178 mg/L) (PubChem 2022a; 2022b), similar changes may have occurred but were less pronounced. An interfacial film between the bulk bituminous and aqueous phases may also explain these observations. Such films have been observed to have higher aqueous and medium/heavier hydrocarbon (e.g., 1-MN) concentrations and lighter hydrocarbon (e.g., o-xylene) concentrations in aqueous/coal tar systems (Nelson et al. 1996). The results are consistent as similar apparent equilibria (the pre-replacement and post-replacement simulated OSTP pore water trials) were significantly lower than the “forced equilibrium” values (Figure 4.4) with T-test p-values <α=0.05 (Tables A4.4 and A4.5).

The post-replacement trials also showed higher repeatability with errors ~one order of magnitude lower than the pre-replacement trials (all performed in triplicate). The error was expected to be the same with the same sampling and fluorescence methods. This decrease in error may be due to the formation of an interfacial film or the intra-bitumen concentration gradients, limiting mass transfer consistently.

4.3.3.2.1 Varying Mass Transfer Properties

As described in section 4.3.3.1.1, these experiments are abiotic, hence if the bitumen droplet is well-mixed (i.e., no intra-NAPL mass transfer limitations), the mass transfer of naphtha from the bitumen to the aqueous phases can be described using (4.1), where “p” is 1 and a single value of λ_i per trial is used. Similarly to initially homogenous bitumen droplet experiments (Figure 4.6), this was not the case; the plots of 1 – CW/Cw(eq) vs. t for each post-aqueous phase replacement trial were fitted with λ_i parameters, and the results varied considerably (Figure 4.8).
Figure 4.8: Integrated mass transfer data for the post-replacement sessile bitumen droplet experiments (equation (4.2)) of (a) 2 wt.% o-xylene in RO water and (b) 4 wt.% 1-MN in OSTP pore water. These two datasets are representative of all the trials performed (Figure A4.4). All data sets were fitted with a single lumped mass transfer coefficient ($\lambda_i$) (equation (4.2)) and two distinct mass transfer coefficients ($\lambda_i$), indicating a change in mass transfer properties over time.

No trend was fully described using a single $\lambda_i$ value (Figure 4.8). While the regression of the data sets resulted in some strong correlations (the 4% o-xylene and 4% 1-MN trials in simulated OSTP pore water with $R^2$ values of 0.971 and 0.855, respectively), there was still a large discrepancy between the predicted and experimental values within the first 10 d for all data set with a better agreement occurring around 30 days (as indicated by the residuals in Figure A4.5). However, there appeared to be consistent trends with the residuals of these $\lambda_i$ models fitted to the experimental data. Both the single $\lambda_i$ fit and the second of the two $\lambda_i$ fit residuals exhibited almost parabolic behaviour for both RO water trials, with large negative or near zero residuals increasing over time before decreasing again. The first of the two $\lambda_i$ fits seemed evenly distributed around the x-axis (Figure A4.5). All $\lambda_i$ models with the simulated OSTP pore water trials started with larger positive residuals, which decreased over time.

In Figure 4.8, the experimental results for o-xylene with simulated OSTP pore water were best described with a single $\lambda_i$ value of all the post-replacement data sets, followed by the 1-MN in simulated OSTP pore water, then o-xylene and 1-MN in RO water. However, when fitting two distinct $\lambda_i$ values to the data, the all-data sets (besides 1-MN in RO water) yielded stronger correlations. Furthermore, the time
in which the second parameter was used was within the same four – 15 d observed in the pre-replacement experiments. While the single $\lambda_i$ fits were not as poor in the post-replacement experiments, it is still worth noting the improvement when using a two $\lambda_i$ fit. The $\lambda_i$ and $R^2$ values for all the aqueous phase replaced experiments can be seen in Table A4.1.

Table 4.2: Summary of the lumped mass transfer parameters fit for the post-replacement data in Figure A4.4. All data sets had a single $\lambda_i$ fit for the entire data set (single $\lambda_i$ fit), or two $\lambda_i$s applied to two distinct parts of the data set (two $\lambda_i$ fit), the second $\lambda_i$ of the two $\lambda_i$ fit has a coefficient (equation (4.2)). Underlined values were manually fit using statistical definitions and maximizing $R^2$.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Single $\lambda_i$ Fit</th>
<th>Two $\lambda_i$ Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_i$ (d$^{-1}$)</td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td>$\lambda_i$ #1 (d$^{-1}$)</td>
<td>$R^2$ #1</td>
</tr>
<tr>
<td>RO Water Replacement 2% O-Xylene</td>
<td>0.019</td>
<td>0.757</td>
</tr>
<tr>
<td>RO Water Replacement 2% 1-MN</td>
<td>0.012</td>
<td>0.161</td>
</tr>
<tr>
<td>Simulated OSTP Pore Water Replacement 4% O-Xylene</td>
<td>0.021</td>
<td>0.971</td>
</tr>
<tr>
<td>Simulated OSTP Pore Water Replacement 4% 1-MN</td>
<td>0.017</td>
<td>0.855</td>
</tr>
</tbody>
</table>

With the simulated OSTP pore water post-replacement experiments, the single $\lambda_i$ parameter fit the data much better than the pre-replacement, with $R^2$ values of 0.971 and 0.855 compared to 0.523 to 0.803. This better single $\lambda_i$ parameter fit may imply that the phenomena contributing to the reduced mass transfer rates throughout the pre-replacement trials had decreased. In addition, the lumped mass transfer coefficients also decreased for the 2 wt.% RO water trials (0.697 and 0.080 d$^{-1}$ to 0.19 d$^{-1}$ and 0.595 and 0.025 d$^{-1}$ to 0.012 d$^{-1}$ for o-xylene and 1-MN, respectively) indicating the mass transfer rate has also decreased.

The simulated OSTP pore water trials had comparable pre-replacement and post-replacement coefficients ($\lambda_i$ values of 0.029 and 0.0011 d$^{-1}$ to 0.076 and 0.015 d$^{-1}$ for 4 wt.% o-xylene, and 0.076 and 0.01 d$^{-1}$ to 0.037 and 0.017 d$^{-1}$ for 4 wt.% 1-MN). While a similar comparison can be made for these trials, the high discrepancy between the predicted and observed concentrations shows that these simplified equations need to be revised for modelling these systems. These revisions could include modelling
interfacial film phenomena between the bitumen droplet and aqueous phase or the diffusion of naphtha surrogates within a bitumen droplet.

4.3.4 Comparison of Biodegradation and Mass Transfer Rates

Biodegradation rates were taken from biodegradation studies of naphtha or similar compounds. As conditions vary between studies and over time, maximal rates were taken and converted to mmol of naphtha and/or naphtha surrogates consumed per week. As degradation rates are often reported on a volumetric basis, they were converted to a total rate of mmol/week using the volumes used in the studies. All the biodegradation rates fall between $9.66 \times 10^{-6}$ to $1.24 \times 10^{-1}$ mmol/week.

Table 4.3: Summary of biodegradation rates of naphtha and/or naphtha surrogates normalized to 23 mL working volume, with their inoculum source and references.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Rates (mmol/week)</th>
<th>Inoculum Source</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-xylene w/ naphtha</td>
<td>$1.92 \times 10^{-3}$</td>
<td>methanogenic OSTP MFT</td>
<td>(Siddique et al. 2008)</td>
</tr>
<tr>
<td>o-xylene w/ BTEX</td>
<td>$4.32 \times 10^{-3}$</td>
<td>methanogenic OSTP MFT</td>
<td>(Meckenstock et al. 2004)</td>
</tr>
<tr>
<td>methyl naphthalene</td>
<td>$7.08 \times 10^{-5}$</td>
<td>sulfate and marine sediment</td>
<td>(Meckenstock et al. 2004)</td>
</tr>
<tr>
<td>naphthalene</td>
<td>$1.77 \times 10^{-5}$</td>
<td>nitrate aquifer</td>
<td>(Meckenstock et al. 2004)</td>
</tr>
<tr>
<td>naphthalene</td>
<td>$1.24 \times 10^{-1}$</td>
<td>nitrate river sediment</td>
<td>(Meckenstock et al. 2004)</td>
</tr>
<tr>
<td>naphthol</td>
<td>$1.35 \times 10^{-3}$</td>
<td>methanogenic soil</td>
<td>(Meckenstock et al. 2004)</td>
</tr>
<tr>
<td>acenaphthene</td>
<td>$9.66 \times 10^{-6}$</td>
<td>nitrate uncontaminated soil</td>
<td>(Meckenstock et al. 2004)</td>
</tr>
<tr>
<td>Naphthalene, high concentration</td>
<td>$3.5 \times 10^{-4}$</td>
<td>methanogenic soil</td>
<td>(Kong et al. 2019)</td>
</tr>
<tr>
<td>naphthalene</td>
<td>$5.46 \times 10^{-5}$</td>
<td>methanogenic soil</td>
<td>(Kong et al. 2019)</td>
</tr>
</tbody>
</table>

While diffusion is not necessarily linearly scalable depending on bitumen droplet geometry and interfacial surface area, the maximal mass transfer rates from the sessile diffusional experiments in section 4.3.3 were taken and converted to mmol/week for the geometry of the reactors used in this work (Table 4.4).
Table 4.4: Summary of mass transfer rates of naphtha surrogates normalized to the geometry of the experimental reactors (a 23 mL working volume and a surface area (SA) of 3.14 cm²).

<table>
<thead>
<tr>
<th>o-xylene</th>
<th>mmol/week</th>
<th>1-MN</th>
<th>mmol/week</th>
</tr>
</thead>
<tbody>
<tr>
<td>4% spiked high</td>
<td>1.05x10⁻⁷</td>
<td>4% spiked high</td>
<td>2.18x10⁻⁷</td>
</tr>
<tr>
<td>4% spiked low</td>
<td>4.37x10⁻⁸</td>
<td>4% spiked low</td>
<td>2.18x10⁻⁸</td>
</tr>
<tr>
<td>2% spiked high</td>
<td>8.74x10⁻⁷</td>
<td>2% spiked high</td>
<td>4.37x10⁻⁷</td>
</tr>
<tr>
<td>2% spiked low</td>
<td>4.37x10⁻⁸</td>
<td>2% spiked low</td>
<td>2.18x10⁻⁸</td>
</tr>
</tbody>
</table>

These mass transfer rates (ranging from 2.18x10⁻⁸ to 8.74x10⁻⁷) are several orders of magnitude lower than published biodegradation rates for the specific geometry studied in this work. While there are shortcomings when comparing literature biodegradation rates to experimental mass transfer rates, it is clear that under these assumptions, the rate of naphtha surrogate degradation would be severely limited by mass transfer of the surrogates from the bituminous to aqueous phase. Consequently, in the study of naphtha (or similar) biodegradation rates in the presence of bitumen, the mass transfer effects of naphtha (or similar compounds) from bituminous to aqueous phase must at the very least be considered.

4.4 Conclusions

To study the mass transfer properties of naphtha from bituminous to aqueous phases, the bitumen froth was processed for experimental repeatability and then characterized. Bitumen was spiked with 0, 1, 2, 3, or 4 wt.% of o-xylene and 1-MN, which were chosen to represent naphtha. All experiments had ~0.5 g bitumen droplets in the bottom of ~21 mL scintillation vials filled with an aqueous phase (RO water or a saline simulated oil sands tailings pond (OSTP) pore water solution). Vials were agitated (forced equilibrium), stored still to be sacrificially sampled over time (sessile diffusional experiment), or stored in still conditions then have the aqueous phase replaced after equilibrium was reached to again be sacrificially sampled over time (aqueous phase replacement).

Forced equilibrium experiments showed a linear increase of the aqueous concentration of the naphtha surrogates as a function of its mole fraction solubilized in a submerged bitumen droplet at low
mole fractions. Using simulated OSTP pore water solution resulted in concentrations approximately half of those observed in comparable experiments using reverse osmosis water.

A combined empirical and theoretical fugacity model provided insight into these systems and indicated that equilibrium was reached. However, the model was not found to be robust. While it accurately predicted two of the four data sets (1-MN with RO water and o-xylene with simulated OSTP pore water), it greatly under-estimated the o-xylene concentrations in RO water and over-estimated the 1-MN concentrations in simulated OSTP pore water. Lighter residual hydrocarbons from the bitumen not detected by the fluorescence analysis may have contributed to a significant reduction in the observed aqueous equilibrium concentration compared to the theoretical concentration for a pure component.

In diffusional mass transfer experiments, bitumen droplets were spiked with naphtha surrogates and submerged in water under sessile conditions, and the aqueous phase was sacrificially sampled for analysis over time. A steep increase in the aqueous surrogate concentration was observed over seven to 30 days, after which an apparent equilibrium was reached. This equilibrium was achieved faster with RO water and initially homogenous bitumen droplets (~1-2 weeks). Conversely, trials with simulated OSTP pore water and potentially non-homogenous bitumen droplets were significantly slower (~3-4 weeks). The initial concentration of the naphtha surrogate within the bitumen droplet (2 wt.% vs 4 wt.%) has minimal impact on the rates that the concentrations increased in the aqueous phase and on the apparent aqueous equilibrium concentrations. Because of their properties, the equilibrium concentrations of o-xylene were typically an order of magnitude higher than those observed for 1-MN. The salts in the simulated OSTP pore water halved the apparent equilibrium concentrations for o-xylene compared to RO water. However, the 1-MN concentrations in simulated OSTP pore water were approximately six times lower than in RO water. The forced equilibrium experimental findings and the thermodynamic fugacity-based model did not predict this reduced equilibrium, indicating possible mass transfer limitations and/or other non-fluorescent bituminous compounds saturating the aqueous phase. In RO water the 1-MN “apparent equilibria” achieved were higher than the forced equilibria concentrations (with only minimal differences for o-xylene) could be due to the
agitation of the forced equilibria experiments solubilizing non-fluorescent bituminous compounds to artificially higher aqueous concentrations than they would typically exist at static equilibria. If this occurred, it is possible that those artificially higher concentration compounds were more soluble than 1-MN, effectively occupying the aqueous phase and limiting the amount 1-MN which can be solubilized.

While conditions and specific geometries can vary greatly, in this context (~0.5 g bitumen droplet, ~3.14 cm$^2$ interfacial surface area, and a 23 mL working aqueous volume) the mass transfer rate may be one to seven orders of magnitude slower than the biodegradation. While this is a large range, it indicates that mass transfer effects cannot be ignored in the study of naphtha biodegradation in the MFT of OSTPs.

A lumped mass transfer rate coefficient was applied to the concentration profiles of all the experimental data but proved unsatisfactory. Assuming that the basis of concentration gradients at the aqueous phase boundary layer (next to the bitumen-aqueous interface) as a driving force for mass transfer holds, the mass transfer rate coefficient decreases over time as the bulk aqueous phase concentration increases. While it may not necessarily link directly to a physical phenomenon, the RO water trials with an initial homogenous bitumen droplet were well characterized with two distinct mass transfer coefficients. The first coefficient was applicable at 0-4 days in the experiment, while the second coefficient was an order of magnitude lower and was applied at > 4 days. While not as good a fit, this trend was also observed with simulated OSTP pore water. It is hypothesized that the apparent decrease in the accurate mass transfer rate coefficient (after 4-15 days) was due to naphtha surrogate concentration gradients developing within the bitumen droplets such that the layers of bitumen near the bitumen-aqueous interface had severely reduced concentrations hence lowering mass transfer rates. The other explanation may be the formation of an interfacial film at the bitumen-aqueous interface that impedes mass transfer. The existence of an interfacial film is supported by the two distinct coefficients being a better fit for experimental data from the trials with homogenous initial bitumen droplets. A film forming would likely not be an instantaneous event causing this phenomenon. Both explanations are supported by the fact that the diffusional mass transfer experiments in which the aqueous phases of the reactors were replaced after an apparent equilibrium was reached were
accurately described with a single lumped mass transfer rate coefficient comparable to the second of the two coefficients applied in the pre-replacement experiments.

4.5 References


Moe, J. (2021). *Using fluorescence spectroscopy to measure the biodegradation of naphtha in Athabasca oil sands tailings ponds* [MSc]. Queen’s University.


Pierfelice, K. N. (2013). *Effects of salinity on productivity and biogeochemical processes in tidal freshwater and oligohaline wetlands of south carolina, USA.*


   https://pubchem.ncbi.nlm.nih.gov/compound/o-Xylene#section=Flash-Point


Chapter 5

Conclusions and Recommendations

5.1 Summary and Conclusions

The Athabascan oil sands are of great concern as they play a key role in Canada’s socioeconomics (Small et al. 2015; Lo et al. 2006). The biogenic greenhouse gas emissions (GHGs), CH$_4$ and CO$_2$ from this industry are significant and must be better understood.

To address overall research objective (1), a fluorescence spectroscopy method was developed to improve the analysis of the naphtha surrogates, o-xylene and 1-methylnaphthalene (1-MN). MeOH was used as a co-solvent to reduce the volatilization of o-xylene and 1-MN samples in aqueous solutions. A 20 vol.% solution was chosen as it was the highest tested concentration which reduced volatilization the most. This method works in the presence of bituminous components, provided the contribution of bitumen to the fluorescence signal is tracked. It is recommended that signals from naphtha-negative, bituminous-positive controls are subtracted from the signals of the naphtha surrogate samples. Bitumen affected the linearity and minimum observed concentration but had little or no impact on naphtha surrogate volatilization. The minimum observed concentrations were still sufficient in the presence of bitumen, ranging from 100 µg/L - 1 mg/L and 10 - 100 µg/L for o-xylene and 1-MN, respectively. The linear ranges were also acceptable, with the highest measurable concentrations ranging from 25-100 mg/L for o-xylene and 5-10 mg/L for 1-MN. The naphtha surrogates (o-xylene and 1-MN) are expected to be at a ~10:1 molar ratio in aqueous solution when added as a separate non-aqueous phase in quantities that exceed the aqueous samples’ maximum solubility. Hence this method was developed at this ratio where no interference of the fluorescence signals was observed. A simulated OSTP pore water solution decreased the linear range of fluorescence, but a calibration curve using simulated pore water with 20% MeOH yielded a similar performance as RO water, also with 20% MeOH. If experiments use a saline solution or are performed in
such a way that ratios of o-xylene:1-MN differ from 10:1 significantly (e.g., 1:1 or 100:1), it is recommended that new calibration curves be generated under these conditions for sufficient performance.

The fluorescence spectroscopy method was used to analyze the supernatant of repeated extractions of mature fine tailings (MFT) samples with RO water and 20% HPLC grade MeOH. MFT samples initially spiked with o-xylene showed that partition coefficients can be determined for naphtha surrogates between the “solids” of MFT (bitumen, sands, silts, and clays) and the aqueous phase. However, the total organic carbon content (of the solids after the extractions) showed that the variance between pond samples was so high that the applicability of any acquired coefficients would be limited. Due to the partitioning between the MFT “solids” and the aqueous phase, only general changes in naphtha surrogate concentration or differences between similar samples can be tracked in the whole MFT samples and not the specific phases within the MFT sample. Nevertheless, the method was an accurate, reliable, cheap, and quick analytical way to determine the aqueous concentrations of naphtha surrogates in the mass transfer experiments.

To study the mass transfer properties of naphtha from bituminous to aqueous phases, bitumen was extracted from bitumen froth. Bitumen droplets (~0.5 g) spiked with 0, 1, 2, 3, or 4 wt.% o-xylene and 1-MN were placed in the bottom of 24 mL scintillation vials filled with RO water or simulated OSTP pore water. Three experiments were performed with these vials where they were either agitated (forced equilibrium regarding research objectives (2) and (3)) or stored with no mixing (sessile diffusional experiment (2)), or stored with no mixing until equilibrium was reached, then the aqueous phase was replaced after which they were sacrificially sampled over time (aqueous phase replacement (3)).

The forced equilibrium experiments showed a linear increase of the surrogate’s aqueous phase concentration with respect to the initial mole fraction solubilized in a bitumen droplet for the spiked bitumen concentrations tested. The concentrations observed in RO water were approximately double that of the simulated OSTP pore water solution. A pre-existing combined empirical and theoretical fugacity model indicated that equilibrium was likely reached in these systems. However, the model was not robust enough to replace the need for experimental data.
In the diffusional mass transfer experiments, the aqueous phase concentrations of the naphtha surrogates increased steeply over the first ~1-2 weeks, after which an apparent equilibrium was reached. The apparent equilibria were achieved faster with RO water than in simulated OSTP pore water trials. The initial amount of naphtha spiked into the bitumen (2 and 4 wt.%) had minimal impact on the equilibrium concentrations and the time to achieve it. O-xylene concentrations were ~ an order of magnitude higher than 1-MN, and the simulated OSTP pore water reduced the apparent equilibria by two – six times compared to RO water. The combined theoretical and empirical fugacity-based model and the forced equilibrium experiments did not correctly predict these equilibria concentrations.

Similar (RO water) or lesser (simulated OSTP) equilibrium concentrations were observed for the aqueous phase replacement experiments compared to the other sessile diffusional experiments. These equilibria also took longer (~3-4 weeks). Regarding research objective (3), for the sessile diffusional and aqueous phase replacement experiments, a single lumped mass transfer rate coefficient was applied to the concentration profiles but proved unsatisfactory. While not necessarily linked to a distinct physical phenomenon, two lumped mass transfer rate coefficients were applied over two separate time ranges to accurately describe the data. These coefficients decreased over time, where the first coefficient was applied to ~4-15 days and the second applied > 15 days, indicating an unaccounted-for phenomenon limiting the mass transfer of the naphtha surrogates. It is hypothesized that the limiting phenomenon may be due to diffusional mass transfer limitation within the bitumen droplet or the formation of an interfacial film at the bitumen-aqueous interface. The existence of bituminous mass transfer limitations and/or an interfacial film is supported by a better fit of single, lumped mass transfer rate coefficients for the aqueous phase replacement experiments.

While conditions and specific geometries can vary greatly when comparing maximal experimental mass transfer rates and maximal literature biodegradation rates, in the context of ~0.5 g bitumen droplet with a ~3.14 cm² interfacial surface area to a static 23 mL aqueous phase, the mass transfer rate may be severely impairing biodegradation rates. The dissolution of naphtha from bitumen to the aqueous phase in
this context may be one to seven orders of magnitude lower than the biodegradation. While the large range of results can be affected by various conditions, this indicates that mass transfer effects cannot be ignored in the study of naphtha biodegradation in the MFT of OSTPs.

5.2 Contributions

This work contributed to the OSTP naphtha-related research by developing a quick and reliable analytical fluorescence spectroscopy to detect aqueous phase concentrations of single and two-ring aromatic compounds. Interference from bitumen, salts, other naphtha surrogates and MFT can be controlled to varying degrees in laboratory settings. This reduces the barrier to entry for similar OSTP research using naphtha surrogates, potentially making studies of high interest and value more common. However, the analytical interference is reduced with naphtha-negative bituminous and MFT controls, and calibrations for pre-determined salt concentrations. Hence, the applications of this method in the field where variables cannot be controlled will limit its precision. Yet with its low cost and speed of analysis, it could be used (or modified for use) to track large general changes over time when moderate precision is required.

This work contributes a unique determination of the mass transfer properties of naphtha surrogates from bituminous to aqueous phases. Furthermore, its findings can be used to make a multicomponent diffusional model. Industrial experts can use these models to inform their decisions around the treatment/remediation of their tailings and guide their directions for future research topics regarding the Athabascan OSTPs.

5.3 Recommendations for Future Work

More research is required to understand the biogenic GHG emissions from the MFT within the Athabascan OSTPs. The fluorescence method developed in this work could aid in this research. For example, repeated extractions of MFT samples (spiked with a naphtha surrogate) with RO water or 20% HPLC grade MeOH and analysis of the supernatant can be used to derive partition coefficients of naphtha surrogates between the “solids” of MFT (bitumen, sands, silts, and clays) and the aqueous phase. While the precise applicability
of these coefficients depends on the specific MFT sample and extraction solution used, relative partitioning of naphtha surrogates can be determined to gain more insight into naphtha behaviour.

Investigations into other analytical methods may be beneficial as different studies may have different requirements, and more resources may be available. For example, using solid phase microextraction (SPME) with a siloxane polymer and subsequent analysis of naphtha may prove useful when not interested in studying the partitioning behaviour between phases or when dealing with only dilute samples (Moe 2021). The fluorescence spectroscopy method was developed for a specific application and to be timely and affordable, hence if more precision is required, time and finances are not a concern and/or a compositional analysis of naphtha is preferred over naphtha surrogates, other analytical methods should be investigated.

The mass transfer of naphtha from the bituminous to aqueous phases and the equilibrium concentrations achieved were significantly lower than theoretical and forced equilibrium concentrations. This indicates possible mass transfer limitations and/or some lighter residual non-fluorescent bituminous compounds saturating the aqueous phase. Hence future work should perform some additional compositional analysis on the background bituminous contamination. More research should be conducted into mass transfer limitations due to concentration gradients developing within the bitumen droplets such that the outer layers of droplets are depleted of naphtha surrogates. Investigations should also be performed on the formation of an interfacial film at the bitumen-aqueous interface, which may impede mass transfer. The data from this work on bitumen characterization, forced equilibrium, and all the sessile diffusion mass transfer experiments should be used to fit a model capable of describing the diffusional phenomena changing over time within a bitumen droplet and how the environment outside of the droplet impacts it. While not presented in this work, this is currently being pursued, and this model is being used to form a wide variety of predictions to inform decisions on this subject.

Only the mole fraction of the naphtha surrogate in bitumen, the presence and absence of salinity, and aqueous phase replacement was varied in this work. While this was relevant for goals of this work, to
develop a better understanding of mass transfer phenomena in the OSTPs in general, experiments would be required that isolate properties not varied in this work such as bitumen geometry, bitumen viscosity.

The bitumen found in the OSTPs ranges from micro-droplets to slicks of several meters. Hence, it is recommended that more research towards a more accurate understanding of the OSTP (primarily the MFT) constituents and properties (e.g., bitumen dispersion) be performed to fill this significant knowledge gap and provide insight into the overall problem. Experiments should be performed under a few of these conditions to prove the model’s validity in informing OSTP reclamation decision-making.

The model being developed could be combined with known biodegradation data (e.g., literature biodegradation rates) to predict under which conditions biogenic GHG production is limited by naphtha mass transfer. Preliminary biodegradation studies (not presented in this work) were begun to evaluate the mass transfer predictions. These should be continued, and it is recommended that these experiments include varying degrees of mass transfer limitations (including different droplet sizes, naphtha surrogate concentrations spiked in the bituminous and aqueous phases, and mixing) with microbial populations derived from OSTP MFT to study the effects of mass transfer on naphtha biodegradation.

5.4 References


Reference List


Ortega-Calvot, Jose-Julio, and Martin Alexander. 1994. “Roles of Bacterial Attachment and Spontaneous Partitioning in the Biodegradation of Naphthalene Initially Present in Non-Aqueous-


Pierfelice, Kathryn Noel. 2013. “Effects of Salinity on Productivity and Biogeochemical Processes in Tidal Freshwater and Oligohaline Wetlands of South Carolina, USA.”


Sean Wells, Patrick. 2011. “Long Term In-Situ Behaviour of Oil Sands Fine Tailings in Suncor’s Pond 1A.” In Tailing and Mine Waste Conference 2011. Vancouver, BC (Canada): AMEC (United Kingdom); Golder Associates (United States); Norwest Corporation (Canada); Rescan Environmental Services Ltd. (Canada); Ausenco (Australia). https://doi.org/10.14288/1.0107699.


Appendices

Appendix For Chapter 3

Figure A3.1: 1-MN calibration curves for the integrated ranges of 315-410nm (in RO water).
Figure A3.2: The fluorescence emission spectra for toluene (d), o-xylene (b), and 1-MN (c) are shown when excited at 260 nm in an aqueous solution. An anthracene standard ((a) used for device calibration) fluorescence emission spectra is shown (top right) when excited at 310 nm.
Figure A3.3: Integrated areas from fluorescence analysis of o-xylene and 1-MN in 20% MeOH and RO water at ~ 5 min intervals.

Figure A3.4: Fluorescence spectroscopy responses of microcosms enriched with naphtha, toluene and 1-MN or o-xylene and 1-MN.
Figure A3.5: Integrated fluorescence responses of o-xylene at different ratios with 1-MN (left) and 1-MN when at different ratios with o-xylene.
Figure A3.6: Calibration curves of o-xylene and 1-MN in solutions with “background” bitumen signal solutions in 20% MeOH in RO water to ensure the linearity of a fluorescence response still occurs in the presence of other bituminous molecules when excited at 260 nm.
Figure A3.7: Fluorescence emission spectra of serial dilution of o-xylene and 1-MN in simulated OSTP pore water with 20 vol.% HPLC grade MeOH. (a) shows 4 dilutions of o-xylene and 1-MN at a 10:1 ratio (o-xylene concentration stated first, 1-MN stated second) along with a blank solution with no o-xylene or 1-MN. (b) contains no new information but is zoomed in at the lowest two concentrations, and the solvent blank with a different y-axis to visualize the data better.

Figure A3.8: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment only using 20% MeOH on Pond B - 12.5 m samples.
Figure A3.9: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment only using 20% MeOH on Pond A - 5 m samples.

Figure A3.10: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment on Pond B - 12.5 m samples.
Figure A3.11: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment on Pond A - 15 m samples.

Figure A3.12: Aqueous phase 1-ring aromatic concentrations from MFT centrifugation and rinsing experiment on Pond A - 5 m samples.
Figure A3.13: Calibration curves for (a) o-xylene and (b) 1-MN in the simulated OSTP pore water with both the linear ranges that were used for the calibration curves and non-linear ranges which were omitted for the calibration curves.

Appendix For Chapter 4

A temperature range of 80-85°C was selected based on a study which evaluated weight loss due to volatilization from heating and mixing (Table A4.1). 1 g each of toluene, o-xylene, nonane and 1-MN (the balance was accurate to 0.0001 g) were added to ~25 g of bitumen and heated at different temperatures for 15 min. Due to the high viscosity of the bitumen (874 Pa s at 20°C, section 4.3.1), the highest temperature without any significant loss was selected to ensure homogeneity of the spiked bitumen sample after 5 min of vortexing.
Table A4.1: Weight retained for 1 g each of toluene, o-xylene, nonane and 1-MN were added to ~25 g of bitumen in a sealed glass vial after heating at different temperatures for 30 min and 5 min of mixing.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>% Weight Retained After Heating Spiked Bitumen</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>~100</td>
</tr>
<tr>
<td>80</td>
<td>~100</td>
</tr>
<tr>
<td>85</td>
<td>99.95</td>
</tr>
<tr>
<td>90</td>
<td>99.80</td>
</tr>
<tr>
<td>95</td>
<td>97.62</td>
</tr>
<tr>
<td>98</td>
<td>96.89</td>
</tr>
</tbody>
</table>

Table A4.2: Viscosities of bitumen spiked with 0, 1, 2, or 4 wt.% o-xylene and 1-MN and of bitumen alone was analyzed using a REOLOGICA Instruments AB rotational viscometer with a 1 mm gap to a 25 mm radius ETC plate. After sample trimming, the heater casing was closed around the plate and set to 20, 30, or 40°C for 120 s. Once the loading force dropped below 4.074 x 10⁴ Pa or after 300 s (whichever came first), the gap was set to 1.005 mm for a final sample trimming. After trimming, the gap was reset to 1 mm, the heater casing re-closed, and after 30 s to establish temperature equilibrium, the rotor was released, and increasing shear was applied until deformation of the bitumen occurred (i.e., a steep decrease in viscosity as a function of shear rate).

<table>
<thead>
<tr>
<th>Mixture of Bitumen containing o-xylene and 1-MN (wt.%)</th>
<th>Viscosity [Pa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>0 wt.%</td>
<td>874.0</td>
</tr>
<tr>
<td></td>
<td>846.6</td>
</tr>
<tr>
<td>1 wt.%</td>
<td>424.4</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2 wt.%</td>
<td>164.2</td>
</tr>
<tr>
<td>4 wt.%</td>
<td>11.67</td>
</tr>
<tr>
<td>“As received,” Bitumen</td>
<td>24.5</td>
</tr>
</tbody>
</table>
Figure A4.1: Residual plots from the linear regression of the forced equilibrium experiments (Figure 4.5) for o-xylene (a) and 1-MN (b) in simulated OSTP pore water.
Table A4.3: Summary of f-test and t-test results for evaluating differences in apparent equilibrium values for sessile droplet diffusional and forced equilibrium experiments using RO water. All tests are one-tailed tests; a type 2 test refers to a two-sample equal variance t-test, a type 3 is a two-sample unequal variance test, and α-values for all f and t-tests were 0.05.

<table>
<thead>
<tr>
<th>Trial</th>
<th>F-Test P-value</th>
<th>T-Test Tails</th>
<th>T-Test Type</th>
<th>T-test P-value</th>
<th>Interpretation at α=0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration o-xylene 4 wt.% pre-replacement vs 2 wt.% pre-replacement</td>
<td>0.2759</td>
<td>1</td>
<td>2</td>
<td>0.1268</td>
<td>No statistical difference</td>
</tr>
<tr>
<td>1-MN 4% pre-replacement vs 2% pre-replacement</td>
<td>0.0458</td>
<td>1</td>
<td>3</td>
<td>0.3836</td>
<td>No statistical difference</td>
</tr>
<tr>
<td>o-xylene 2 wt.% pre-replacement vs. Forced Equilibrium o-xyl</td>
<td>0.4206</td>
<td>1</td>
<td>2</td>
<td>0.1581</td>
<td>No statistical difference</td>
</tr>
<tr>
<td>4 wt.% o-xylene pre-replacement vs. Forced Equilibrium</td>
<td>0.2758</td>
<td>1</td>
<td>2</td>
<td>0.0205</td>
<td>4% pre-replacement is statistically &lt; forced equilibrium</td>
</tr>
<tr>
<td>2 wt.% 1-MN pre-replacement vs. Forced Equilibrium</td>
<td>0.4259</td>
<td>1</td>
<td>2</td>
<td>0.0019</td>
<td>2% pre-replacement is statistically &gt; forced equilibrium</td>
</tr>
<tr>
<td>4 wt.% 1-MN pre-replacement vs. Forced Equilibrium</td>
<td>0.1843</td>
<td>1</td>
<td>2</td>
<td>0.0851</td>
<td>No statistical difference</td>
</tr>
</tbody>
</table>
Table A4.4: Summary of f-test and t-test results for evaluating the difference in apparent equilibrium values for sessile droplet diffusional and forced equilibrium experiments using simulated tailing pond pore water. All tests are one-tailed; a type 2 test refers to a two-sample equal variance $T$-test, a type 3 is a two-sample unequal variance test, and $\alpha$-values for all $F$ and $T$-tests were 0.05.

<table>
<thead>
<tr>
<th>Trial</th>
<th>F-Test P-value</th>
<th>T-Test Tails</th>
<th>T-Test Type</th>
<th>T-test P-value</th>
<th>Interpretation at $\alpha=0.05$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 wt.% o-xylene Forced vs. Diffusional Equilibrium</td>
<td>0.0656</td>
<td>1</td>
<td>2</td>
<td>0.00001</td>
<td>4 wt.% forced equilibrium is statistically HIGHER than the 4 wt.% diffusional equilibrium for o-xylene</td>
</tr>
<tr>
<td>4 wt.% 1-MN Forced vs. Diffusional Equilibrium</td>
<td>0.0142</td>
<td>1</td>
<td>3</td>
<td>0.0242</td>
<td>4 wt.% forced equilibrium is statistically HIGHER than 4 wt.% diffusional equilibrium for 1-MN</td>
</tr>
</tbody>
</table>

Table A4.5: Summary of F-test and T-test results in evaluating differences in apparent equilibria for sessile droplet diffusional replacement of the aqueous phase " experiments and forced equilibria experiments using simulated OSTP pore water. All tests are one-tailed tests; a type 2 test refers to a two-sample equal variance $T$-test, a type 3 is a two-sample unequal variance test, and $\alpha$-values for all $F$ and $T$-tests were 0.05.

<table>
<thead>
<tr>
<th>Trial</th>
<th>F-Test P-value</th>
<th>T-Test Tails</th>
<th>T-Test Type</th>
<th>T-test P-value</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-replacement vs. post-replacement o-xylene</td>
<td>0.010</td>
<td>1</td>
<td>3</td>
<td>0.3448</td>
<td>There is no statistical difference</td>
</tr>
<tr>
<td>Post-replacement vs. pre-replacement 1-MN</td>
<td>0.3630</td>
<td>1</td>
<td>2</td>
<td>0.3586</td>
<td>There is no statistical difference</td>
</tr>
<tr>
<td>Forced equilibrium vs. post-replacement 4% o-xylene</td>
<td>0.0048</td>
<td>1</td>
<td>3</td>
<td>0.0047</td>
<td>The forced equilibrium concentration is statistically HIGHER than the 4% diffusional post-replacement equilibrium</td>
</tr>
<tr>
<td>Forced equilibrium vs. post-replacement 4% 1-MN</td>
<td>0.0587</td>
<td>1</td>
<td>2</td>
<td>0.0035</td>
<td>The forced equilibrium concentration is statistically HIGHER than the 4% diffusional post-replacement equilibrium</td>
</tr>
</tbody>
</table>
Figure A4.2: Integrated mass transfer data for the sessile bitumen droplet experiments (based on equation (4.2)), of 2% o-xylene and 1-MN in RO water (a and b), 4% o-xylene and 1-MN in RO water (c and d), and o-xylene and 1-MN in simulated tailing pond pore water (e and f). All data sets were fitted with a single lumped mass transfer coefficient ($\lambda_\ell$) as described by equation (4.2) and with two distinct mass transfer coefficients ($\lambda_i$) using equation (4.2) indicating a change in mass transfer properties over time.
Figure A4.3: Plots of the residuals between the fitted lambda lumped mass transfer rate models and the experimental aqueous concentrations from the sessile diffusional experiments. Initial bitumen weight fractions of 2% and 4% of o-xylene and 1-MN with a RO water solution and initial 4% fractions of o-xylene and 1-MN are shown with a simulated OSTP pore water.
Table A4.6: Summary of the lumped mass transfer parameters used in equation (4.2) and represented in Figure 4.6. All data sets had a single $\lambda_i$ for the single $\lambda_i$ model, and for the two $\lambda_i$ model, two $\lambda_i$s were used for each distinct part of the data set with the second $\lambda_i$ having a coefficient as described in equation (4.2). Underlined values were manually fit using statistical definitions and maximizing $R^2$.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Naphtha Surrogate</th>
<th>Initial wt.% Spike in Bitumen Drop</th>
<th>Single $\lambda_i$ model</th>
<th>Two $\lambda_i$ model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_i$ (d$^{-1}$)</td>
<td>$R^2$</td>
<td>$\lambda_i$ #1 (d$^{-1}$)</td>
</tr>
<tr>
<td>RO Water</td>
<td>o-xylene</td>
<td>4%</td>
<td>0.045</td>
<td>0.904</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2%</td>
<td>0.13</td>
<td>0.130</td>
</tr>
<tr>
<td></td>
<td>1-MN</td>
<td>4%</td>
<td>0.044</td>
<td>0.972</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2%</td>
<td>0.07</td>
<td>0.687</td>
</tr>
<tr>
<td>Simulated OSTP Pore Water</td>
<td>o-xylene</td>
<td>4%</td>
<td>0.013</td>
<td>0.523</td>
</tr>
<tr>
<td></td>
<td>1-MN</td>
<td>4%</td>
<td>0.01</td>
<td>0.804</td>
</tr>
</tbody>
</table>

Table A4.7: Summary of F-test and T-test results for evaluating the difference in apparent equilibria values for sessile droplet diffusional replacement of aqueous phase experiments and forced equilibria experiments using RO water. All tests are one-tailed tests; a type 2 test refers to a two-sample equal variance T-test, a type 3 is a two-sample unequal variance test and $\alpha$-values for all F and T-tests were 0.05.

<table>
<thead>
<tr>
<th>Trial</th>
<th>F-Test P-value</th>
<th>T-Test Tails</th>
<th>T-Test Type</th>
<th>T-test P-value</th>
<th>Interpretation at $\alpha$=0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-replacement vs. Post-replacement o-xylene</td>
<td>0.3855</td>
<td>1</td>
<td>2</td>
<td>0.0009</td>
<td>The pre-replacement concentrations are significantly HIGHER than the post-replacement</td>
</tr>
<tr>
<td>Post-replacement vs. Pre-replacement 1-MN</td>
<td>0.3546</td>
<td>1</td>
<td>2</td>
<td>0.00001</td>
<td>The pre-replacement concentrations are significantly HIGHER than the post-replacement</td>
</tr>
<tr>
<td>Forced equilibrium vs. Post-replacement o-xylene</td>
<td>0.3226</td>
<td>1</td>
<td>2</td>
<td>0.0009</td>
<td>The post-replacement 2% equilibrium is significantly LESS than the forced equilibrium</td>
</tr>
<tr>
<td>Post-replacement vs. Forced equilibrium 1-MN</td>
<td>0.3095</td>
<td>1</td>
<td>2</td>
<td>0.0006</td>
<td>The post-replacement 2% equilibrium is significantly LESS than the forced equilibrium</td>
</tr>
</tbody>
</table>
Figure A4.4: Integrated mass transfer data for the post-replacement sessile bitumen droplet experiments (based on equation (4.2)), of 2% o-xylene and 1-MN in RO water (a and b), and 4% o-xylene and 1-MN in simulated tailing pond pore water (c and d). All data sets were fitted with a single lumped mass transfer coefficient ($\lambda$) as described by equation (4.2) and also with two distinct mass transfer coefficients ($\lambda_i$) using equation (4.2) indicating a change in mass transfer properties over time.
Figure A4.5: Plots of the residuals between the fitted lambda lumped mass transfer rate models and the experimental aqueous concentrations from aqueous phase replacement experiments. Initial bitumen weight fractions of 2% o-xylene and 1-MN with a clean replaced RO water solution and initial 4% fractions of o-xylene and 1-MN are shown with a clean replaced simulated OSTP pore water phase.
Table A4.8: The variables used in the combined empirical and fugacity-based equilibrium model, and their respective symbols and units are listed here.

<table>
<thead>
<tr>
<th>Variable Name</th>
<th>Symbol</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of any phase C</td>
<td>$C_x$</td>
<td>mol/cm$^3$</td>
</tr>
<tr>
<td>Fugacity Capacity Constant for any phase x</td>
<td>$Z_x$</td>
<td>Mol/cm$^3$/atm</td>
</tr>
<tr>
<td>Volume of any phase x</td>
<td>$V_x$</td>
<td>cm$^3$</td>
</tr>
<tr>
<td>Partition Coefficient of a substance between siloxane and water</td>
<td>$K_{sw}$</td>
<td>unitless</td>
</tr>
<tr>
<td>Partition Coefficient of a substance between octanol and water</td>
<td>$K_{ow}$</td>
<td>unitless</td>
</tr>
<tr>
<td>“a” coefficient for siloxane-water partitioning</td>
<td>$a_{sw}$</td>
<td>unitless</td>
</tr>
<tr>
<td>“b” coefficient for siloxane-water partitioning</td>
<td>$b_{sw}$</td>
<td>unitless</td>
</tr>
<tr>
<td>Partition Coefficient of a substance between bitumen and water</td>
<td>$K_{bw}$</td>
<td>unitless</td>
</tr>
<tr>
<td>“c” coefficient for bitumen-water partitioning</td>
<td>$c_{bw}$</td>
<td>unitless</td>
</tr>
<tr>
<td>“d” coefficient for bitumen-water partitioning</td>
<td>$d_{bw}$</td>
<td>unitless</td>
</tr>
<tr>
<td>Henrys Law Constant for any substance x</td>
<td>$H_x$</td>
<td>atm.m$^3$/mol</td>
</tr>
<tr>
<td>Fugacity of a system</td>
<td>$f$</td>
<td>atm</td>
</tr>
<tr>
<td>Mass of a substance in the aqueous phase</td>
<td>$m_w$</td>
<td>g</td>
</tr>
<tr>
<td>Molecular Weight of a substance</td>
<td>$M_{mass}$</td>
<td>g/mol</td>
</tr>
<tr>
<td>Aqueous Phase equilibrium concentration of a substance</td>
<td>$C_w$</td>
<td>g/cm$^3$</td>
</tr>
</tbody>
</table>
The combined empirical and fugacity-based equilibrium model used by the brown group was based on several equations as outlined in A4.1 (Moe 2021). The equations use the variables from Table A4.8.

(A4.1)

\[ C_x = Z_x V_x \]

\[ \log K_{sw} = a_{sw} \log K_{ow} + b_{sw} \]

\[ \log K_{bw} = c_{bw} \log K_{ow} + d_{bw} \]

\[ Z_w = \frac{1}{H} \]

\[ Z_s = \frac{K_{sw}}{Z_w} \]

\[ Z_b = \frac{K_{bw}}{Z_w} \]

\[ f = \frac{n_{total}}{\sum Z_x V_x} \]

\[ C_w = f Z_w \]

\[ m_w = C_w V_w M_{mass} \]

\[ C_w^* = \frac{m_w}{V_w} \]