12-2008

Modelling Hydrocarbons Transport in the Aquifer of Bu Hasa Field and Evaluation of Remediation Alternatives

Nawal Eisa Saleh Al Junaibi

Follow this and additional works at: https://scholarworks.uaeu.ac.ae/all_theses
Part of the Water Resource Management Commons

Recommended Citation
https://scholarworks.uaeu.ac.ae/all_theses/548

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at Scholarworks@UAEU. It has been accepted for inclusion in Theses by an authorized administrator of Scholarworks@UAEU. For more information, please contact fadl.musa@uaeu.ac.ae.
Modeling Hydrocarbons Transport in the Aquifer of Bu Hasa Field and Evaluation of Remediation Alternatives

A Thesis
Submitted in partial fulfilment for the requirements of the Degree of Master in Water Resources Program

By

Nawal Eisa Saleh Al Junaibi
B.Sc in Chemistry

December 2008
Title:
Modeling Hydrocarbons Transport in the Aquifer of Bu Hasa Field and Evaluation of Remediation Alternatives

Author's Name
Nawal Eisa Saleh Al Junaibi

Supervisor
Dr. Mohamed Mostafa Mohamed
Assistant Professor of Water Resources
Civil and Environmental Engineering Department
College of Engineering
United Arab Emirates University

Co Supervisor
Prof. Mohsen Sherif
Department Chair and Professor of Water Resources
Civil and Environmental Engineering Department
College of Engineering
United Arab Emirates University
Modeling Hydrocarbons Transport in the Aquifer of Bu Hasa Field and Evaluation of Remediation Alternatives

A Thesis submitted to the Deanship of Graduate Studies United Arab Emirates University

In Partial Fulfilment of the Requirements for M.Sc. Degree in Water Resources

Examination Committee

Dr. Mohamed Mostafa Mohamed, Chair
Civil and Environmental Engineering Department
College of Engineering, UAE University
Al Ain, UAE

Prof. Aly I. El-Kadi, External Examiner
Department of Geology and Geophysics
University of Hawai‘i at Manoa
Honolulu, Hawai‘i 96822 USA

Dr. Munjed Maraqa, Internal Examiner
Civil and Environmental Engineering Department
College of Engineering, UAE University
Al Ain, UAE

Approval
Dean of Graduate Studies: Prof. Ben Bennani

United Arab Emirates University
December 2008
Acknowledgment

First and foremost, I would like to give thanks and praise to the Almighty Allah for His grace and blessings throughout the entire thesis. Without Him, this was nothing. During the completion of this thesis, there were many kinds of supports and collaboration I received by quite few people in order to come to fruition. The knowledge gained through this study is very useful to me and relevant to my expected future practice as water quality control coordinator.

I begin my thanks to those who lent their support and expertise to me in the last three years. I would like to thank my thesis supervisor, Dr. Mohamed Mostafa Mohamed, for his guidance. Without his assistance and support in this thesis, it would not have been completed. I am also grateful to my thesis co-advisor, Prof. Mohsen Sherif, for his valuable advices and recommendations during the completion of this thesis. I would like to thank Mr. Rashed Annon, Organization Capability Division Manager, GASCO for giving me the chance to meet Mr. Salem Sayegh, Head of Process Engineering Department, and Mr. Mohamed Abdul Sater, Senior Process Engineering, Engineering and Technical Support Division in GASCO. They provided me with the essential information and reports related to the contamination at Bu Hasa Liquid Recovery Plant.

I owe a gratitude to Eng. Ismail Saeed, who generously spent a lot of time helping me in all AutoCAD drawings and assisting me in the modifications of many figures. His willingness to help at any time is highly appreciated. I would also like to acknowledge all my friends especially Ms. Mona Rashed and Eman Saif for their support and advice. I would like to thank my colleagues, whom always encourage and pray for me.

And lastly, and most importantly, I feel a deep sense of gratitude for my parents, who believed in me. They are supporting and encouraging me continuously to achieve my dreams. They always inspire me to work with a new ambition. I would like to thank my beloved brothers and sisters for their continuous support and encouragement. I am deeply influenced by my brother, Eng. Bader, who was there when I faced problems during the preparation period of this thesis.
Abstract

The release of non-aqueous phase liquids (NAPLs) to groundwater reservoirs is a serious and widespread environmental problem. In 2000, free phase hydrocarbon was discovered in Liwa aquifer under Bu Hasa Liquid Recovery Plant (LRP). Liwa aquifer is a shallow unconfined aquifer and represents the main water supply in the camp area of Bu Hasa field. Dissolved benzene is observed in at least one observation well in the site. This research is conducted to simulate the fate and transport of the dissolved benzene plume in the groundwater of Liwa aquifer using the finite element model (METABIOTRANS).

The main objective of this thesis is to minimize the flux of the dissolved contaminant into the nearest production well downstream of contaminated Liwa aquifer in the camp area. A sensitivity analysis study was performed to assess the sensitivity of the dissolved plume migration to several physical and biological parameters. Results of the sensitivity analysis show that the plume migration is more sensitive to changes in microbial growth rate and substrate half saturation constant and less sensitive to microbial yield factor and dispersion. Different remediation scenarios were performed in which electron acceptor are injected to enhance biodegradation. Remediation scenario with minimum hydrocarbon flux into the camp production wells downstream of the source zone will be suggested as remediation option. The results of the remediation scenarios assured that highest biodegradation rate occurs at injection wells located near the center of the plume where higher contaminant concentrations exist. Placing an injection well near the source zone helps in stimulating the bacterial growth for longer time and therefore, enhances biodegradation. Increasing electron acceptor flux in a well located near the source zone enhances the plume core biodegradation.
# Table of Contents

Acknowledgment
Abstract
Table of contents
List of Figures
List of Tables
List of Symbols

## CHAPTER 1: INTRODUCTION
1.1 Background
1.2 Transport Processes in the Subsurface
1.3 Remediation Technologies
   1.3.1 Chemical Technologies
   1.3.2 Biological Technologies
1.4 Scope and Objectives
1.5 Organization and Contents
1.6 Limitations

## CHAPTER 2: LITERATURE REVIEW
2.1 Mathematical and Numerical Modeling of Hydrocarbon Biodegradation
2.2 Laboratory and Field Studies of Hydrocarbon Bioremediation
2.3 Available Models for Contaminant Fate, Transport and Biodegradation in the Subsurface

## CHAPTER 3: BU HASA LIQUID RECOVERY PLANT
3.1 Site Description and History
3.2 Natural Gas Processing
3.3 Phases of Hydrocarbon in Bu Hasa Field

## CHAPTER 4: MODELING CONTAMINANT TRANSPORT IN LIWA AQUIFER
4.1 Introduction
4.2 METABIOTRANS
   4.2.1 Model Description
   4.2.2 METABIOTRANS Governing Equations
   4.2.3 Input and Output
4.3 Geology of Bu Hasa Field
4.4 Precipitation and Recharge
4.5 Groundwater
4.6 Model Setup
   4.6.1 Model Domain
   4.6.2 Groundwater Flow Model
   4.6.3 Transport Model
4.7 The Base Case

## CHAPTER 5: SENSITIVITY ANALYSIS STUDY OF NATURAL ATTENUATION
5.1 Sensitivity of Natural Attenuation to Changes in Dispersivity
5.2 Sensitivity of Natural Attenuation to Changes in Contaminant Mass Flux
5.3 Sensitivity of Natural Attenuation to Changes in Bacterial Maximum Specific Growth Rate
5.4 Sensitivity of Natural Attenuation to Changes in Initial Biomass Concentration
5.5 Sensitivity of Natural Attenuation to Changes in Bacterial Decay Rate
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6 Sensitivity of Natural Attenuation to Changes in Half Saturation Constant</td>
<td>110</td>
</tr>
<tr>
<td>5.7 Sensitivity of Natural Attenuation to Changes in Microbial Yield Coefficient</td>
<td>118</td>
</tr>
<tr>
<td><strong>CHAPTER 6: ALTERNATIVES FOR REMEDIATION OF CONTAMINATION IN BU HASA FIELD</strong></td>
<td></td>
</tr>
<tr>
<td>6.1 Remediation Scenarios: Group One</td>
<td>142</td>
</tr>
<tr>
<td>6.2 Remediation Scenarios: Group Two</td>
<td>148</td>
</tr>
<tr>
<td>6.3 Remediation Scenarios: Group Three</td>
<td>153</td>
</tr>
<tr>
<td>6.4 Remediation Scenarios: Group Four</td>
<td>158</td>
</tr>
<tr>
<td><strong>CHAPTER 7: SUMMARY, CONCLUSIONS AND RECOMMENDATIONS</strong></td>
<td></td>
</tr>
<tr>
<td>7.1 Summary</td>
<td>172</td>
</tr>
<tr>
<td>7.2 Conclusions</td>
<td>173</td>
</tr>
<tr>
<td>7.3 Recommendations</td>
<td>177</td>
</tr>
<tr>
<td><strong>REFERENCES</strong></td>
<td></td>
</tr>
<tr>
<td><strong>APPENDIX A</strong></td>
<td></td>
</tr>
<tr>
<td><strong>ARABIC ABSTRACT</strong></td>
<td></td>
</tr>
</tbody>
</table>
## List of Figures

| Figure 1.1 | Transport of DNAPL into subsurface (Source: EPA/625-91/028, 1991). |
| Figure 1.2 | The relation between microbial activity and temperature (Source: Suthersan, 1997). |
| Figure 1.3 | Temperature dependency of growth rate of various microorganisms (Source: Suthersan 1997). |
| Figure 1.4 | Chemical oxidation technique (Source: Motsch et al., 2002). |
| Figure 1.5 | Bioventing system (Source: Motsch et al., 2002). |
| Figure 1.6 | Enhanced bioremediation (Source: Motsch et al., 2002). |
| Figure 3.1 | Bu Hasa Liquid Recovery plant location (Source: Forrest and Arnell, 2001). |
| Figure 3.2 | Generalized natural gas processing schematic (Source: Energy Information Administration, 2006). |
| Figure 3.3 | Bu Hasa Liquid Recovery plant (Source: www.gasco.ae, 2008). |
| Figure 3.4 | The dissolved hydrocarbon distribution in former blowdown area (Source: Forrest and Arnell, 2001). |
| Figure 4.1 | The lithology and hydrostratigraphy of Liwa aquifer (Source: Forrest and Arnell, 2001). |
| Figure 4.2 | Groundwater elevation in Bu Hasa Field (Source: Forrest and Arnell, 2001). |
| Figure 4.3 | The site plan of Bu Hasa Liquid Recovery Plant showing the study domain (Source: Forrest and Arnell, 2001). |
| Figure 4.4 | Conceptual cross sectional view of hydrocarbon occurrence (Source: Forest and Arnell, 2001). |
| Figure 4.5 | Discritization of the study domain. |
| Figure 4.6 | Groundwater flow direction in the study domain of Liwa aquifer (Source: Forrest and Arnell, 2001). |
| Figure 4.7 | Benzene plume base case in the absence and presence of bacteria. |
| Figure 4.8 | Biomass contours for the benzene plume base case. |
| Figure 4.9 | The ratio of contaminant mass simulated in the base case in presence and absence of bacteria to the contaminant mass of base case. |
| Figure 5.1 | Effect of decreasing (a) and increasing (b) dispersivity on the contaminant concentration. |
| Figure 5.2 | Effect of decreasing (a) and increasing (b) dispersivity on the biomass concentration after 10 years. |
| Figure 5.3 | Effect of decreasing (a) and increasing (b) dispersivity on the biomass concentration after 20 years. |
| Figure 5.4 | Effect of decreasing (a) and increasing (b) dispersivity on the biomass concentration after 40 years. |
| Figure 5.5 | The ratio of contaminant mass simulated with different dispersivity values to the contaminant mass of base case. |
| Figure 5.6 | Effect of different flux values on contaminant concentration in the presence of bacteria. |
**Figure 5.7** Effect of different flux values on contaminant concentration in the absence of bacteria

**Figure 5.8** Effect of decreasing (a) and increasing (b) $\mu_{\text{max}}$ on the contaminant concentration

**Figure 5.9** Effect of decreasing (a) and increasing (b) $\mu_{\text{max}}$ on the biomass concentration after 10 years

**Figure 5.10** Effect of decreasing (a) and increasing (b) $\mu_{\text{max}}$ on the biomass concentration after 20 years

**Figure 5.11** Effect of decreasing (a) and increasing (b) $\mu_{\text{max}}$ on the biomass concentration after 40 years

**Figure 5.12** The ratio of contaminant mass simulated with different $\mu_{\text{max}}$ values to the contaminant mass of base case

**Figure 5.13** Effect of decreasing (a) and increasing (b) Mo on the contaminant concentration

**Figure 5.14** Effect of decreasing (a) and increasing (b) Mo on the biomass concentration after 10 years

**Figure 5.15** Effect of decreasing (a) and increasing (b) Mo on the biomass concentration after 20 years

**Figure 5.16** Effect of decreasing (a) and increasing (b) Mo on the biomass concentration after 40 years

**Figure 5.17** The ratio of contaminant mass simulated with different Mo values to the contaminant mass of base case

**Figure 5.18** Effect of decreasing (a) and increasing (b) B on the contaminant concentration

**Figure 5.19** Effect of decreasing (a) and increasing (b) B on the biomass concentration after 10 years

**Figure 5.20** Effect of decreasing (a) and increasing (b) B on the biomass concentration after 20 years

**Figure 5.21** Effect of decreasing (a) and increasing (b) B on the biomass concentration after 40 years

**Figure 5.22** The ratio of contaminant mass simulated with different B values to the contaminant mass of base case

**Figure 5.23** Effect of decreasing (a) and increasing (b) $K_s$ on the contaminant concentration

**Figure 5.24** Effect of decreasing (a) and increasing (b) $K_s$ on the biomass concentration after 10 years

**Figure 5.25** Effect of decreasing (a) and increasing (b) $K_s$ on the biomass concentration after 20 years

**Figure 5.26** Effect of decreasing (a) and increasing (b) $K_s$ on the biomass concentration after 40 years

**Figure 5.27** The ratio of contaminant mass simulated with different $K_s$ values to the contaminant mass of base case

**Figure 5.28** Effect of decreasing (a) and increasing (b) $Y_s$ on the contaminant concentration
Figure 5.29  Effect of decreasing (a) and increasing (b) Y\textsubscript{s} on the biomass concentration after 10 years

Figure 5.30  Effect of decreasing (a) and increasing (b) Y\textsubscript{s} on the biomass concentration after 20 years

Figure 5.31  Effect of decreasing (a) and increasing (b) Y\textsubscript{s} on the biomass concentration after 40 years

Figure 5.32  The ratio of contaminant mass simulated with different Y\textsubscript{s} values to the contaminant mass of base case

Figure 5.33  Contaminant concentration simulated with different $\mu_{\text{max}}$ values near source zone

Figure 5.34  Contaminant concentration simulated with different $K_s$ values near source zone

Figure 5.35  Contaminant concentration simulated with different Mo values near source zone

Figure 5.36  Contaminant concentration simulated with different B values near source zone

Figure 5.37  Contaminant concentration simulated with different Y\textsubscript{s} values near source zone

Figure 5.38  Contaminant concentration simulated with different contaminant mass flux values near source zone

Figure 5.39  Contaminant concentration simulated with different dispersivities values near source zone

Figure 5.40  Contaminant concentration simulated with different $\mu_{\text{max}}$ values at plume leading edge

Figure 5.41  Contaminant concentration simulated with different $K_s$ values at plume leading edge

Figure 5.42  Contaminant concentration simulated with different Mo values at plume leading edge

Figure 5.43  Contaminant concentration simulated with different B values at plume leading edge

Figure 5.44  Contaminant concentration simulated with different Y\textsubscript{s} values at plume leading edge

Figure 5.45  Contaminant concentration simulated with different contaminant mass flux values at plume leading edge

Figure 5.46  Contaminant concentration simulated with different dispersivities values at plume leading edge

Figure 6.1  (a) Wells locations in scenarios one, three, five and seven in group one, (b) Wells locations in scenarios two, four, six and eight in group one, (c) Wells locations in scenario sixteen

Figure 6.2  Electron acceptor contour lines (well at y distance of 200 m) in the absence of electron donor and bacteria

Figure 6.3  The contaminant concentration for remediation scenarios of group 1 after 40 years

Figure 6.4  The electron acceptor concentration in scenario 1
Figure 6.5  The biomass growth in scenario 1
Figure 6.6  The ratio of contaminant mass simulated in scenarios of group one to the contaminant mass of base case
Figure 6.7  The contaminant concentration for remediation scenarios of group 2 after 40 years
Figure 6.8  The electron acceptor concentration in scenario 9
Figure 6.9  The biomass concentration in scenario 9
Figure 6.10  The ratio of contaminant mass simulated in scenarios of group two to the contaminant mass of base case
Figure 6.11  The contaminant concentration for remediation scenarios of group 3 after 40 years
Figure 6.12  The electron acceptor concentration in scenario 18
Figure 6.13  The biomass concentration in scenario 18
Figure 6.14  The ratio of contaminant mass simulated in scenarios of group three to the contaminant mass of base case
Figure 6.15  The contaminant concentration for remediation scenarios of group 4 after 40 years
Figure 6.16  The electron acceptor concentration in scenario 26
Figure 6.17  The biomass concentration in scenario 26
Figure 6.18  The ratio of contaminant mass simulated in scenarios of group four to the contaminant mass of base case
Figure 6.19  Contaminant concentration simulated with selected scenarios of group one near source zone
Figure 6.20  Contaminant concentration simulated with selected scenarios of groups one, two and three near source
Figure 6.21  Contaminant concentration simulated with selected scenarios of groups three and four near source zone
Figure 6.22  Contaminant concentration simulated with selected scenarios of group four near source zone
Figure 6.23  Contaminant concentration simulated with selected scenarios of group one at plume leading edge
Figure 6.24  Contaminant concentration simulated with selected scenarios of groups one, two and three at plume leading edge
Figure 6.25  Contaminant concentration simulated with selected scenarios of groups three and four at plume leading edge
Figure 6.26  Contaminant concentration simulated with selected scenarios of group four at plume leading edge
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Advantages and disadvantages of physical techniques</td>
<td>14</td>
</tr>
<tr>
<td>4.1</td>
<td>Input data for biological parameters</td>
<td>70</td>
</tr>
<tr>
<td>4.2</td>
<td>Literature values for biological parameters</td>
<td>71</td>
</tr>
<tr>
<td>5.1</td>
<td>Simulations of sensitivity analysis</td>
<td>77</td>
</tr>
<tr>
<td>6.1</td>
<td>Remediation scenarios of group one</td>
<td>140</td>
</tr>
<tr>
<td>6.2</td>
<td>Remediation scenarios of group two</td>
<td>140</td>
</tr>
<tr>
<td>6.3</td>
<td>Remediation scenarios of group three</td>
<td>141</td>
</tr>
<tr>
<td>6.4</td>
<td>Remediation scenarios of group four</td>
<td>141</td>
</tr>
<tr>
<td>6.5</td>
<td>Bioremediation efficiency of group one</td>
<td>147</td>
</tr>
<tr>
<td>6.6</td>
<td>Bioremediation efficiency of group two</td>
<td>152</td>
</tr>
<tr>
<td>6.7</td>
<td>Bioremediation efficiency of group three</td>
<td>158</td>
</tr>
<tr>
<td>6.8</td>
<td>Bioremediation efficiency of group four</td>
<td>164</td>
</tr>
</tbody>
</table>
List of Tables

Table 1.1  Advantages and disadvantages of physical techniques  14
Table 4.1  Input data for biological parameters  70
Table 4.2  Literature values for biological parameters  71
Table 5.1  Simulations of sensitivity analysis  77
Table 6.1  Remediation scenarios of group one  140
Table 6.2  Remediation scenarios of group two  140
Table 6.3  Remediation scenarios of group three  141
Table 6.4  Remediation scenarios of group four  141
Table 6.5  Bioremediation efficiency of group one  147
Table 6.6  Bioremediation efficiency of group two  152
Table 6.7  Bioremediation efficiency of group three  158
Table 6.8  Bioremediation efficiency of group four  164
List of Tables

Table 1.1 Advantages and disadvantages of physical techniques 14
Table 4.1 Input data for biological parameters 70
Table 4.2 Literature values for biological parameters 71
Table 5.1 Simulations of sensitivity analysis 77
Table 6.1 Remediation scenarios of group one 140
Table 6.2 Remediation scenarios of group two 140
Table 6.3 Remediation scenarios of group three 141
Table 6.4 Remediation scenarios of group four 141
Table 6.5 Bioremediation efficiency of group one 147
Table 6.6 Bioremediation efficiency of group two 152
Table 6.7 Bioremediation efficiency of group three 158
Table 6.8 Bioremediation efficiency of group four 164
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>The power of hydrogen</td>
</tr>
<tr>
<td>E&lt;sub&gt;H&lt;/sub&gt;</td>
<td>Redox potential</td>
</tr>
<tr>
<td>F</td>
<td>Flux of solute</td>
</tr>
<tr>
<td>C</td>
<td>Solute concentration</td>
</tr>
<tr>
<td>D&lt;sub&gt;d&lt;/sub&gt;</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>ω</td>
<td>Tortuosity coefficient</td>
</tr>
<tr>
<td>D'</td>
<td>Effective diffusion coefficient</td>
</tr>
<tr>
<td>v&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Average linear velocity</td>
</tr>
<tr>
<td>K</td>
<td>Hydraulic conductivity</td>
</tr>
<tr>
<td>n&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Effective porosity</td>
</tr>
<tr>
<td>D</td>
<td>Hydrodynamic dispersion coefficient</td>
</tr>
<tr>
<td>D&lt;sub&gt;L&lt;/sub&gt;</td>
<td>Longitudinal hydrodynamic dispersion coefficient</td>
</tr>
<tr>
<td>D&lt;sub&gt;T&lt;/sub&gt;</td>
<td>Transverse hydrodynamic dispersion coefficient</td>
</tr>
<tr>
<td>α&lt;sub&gt;L&lt;/sub&gt;</td>
<td>Longitudinal dispersivity</td>
</tr>
<tr>
<td>α&lt;sub&gt;T&lt;/sub&gt;</td>
<td>Transverse dispersivity</td>
</tr>
<tr>
<td>R</td>
<td>Retardation factor</td>
</tr>
<tr>
<td>ρ&lt;sub&gt;b&lt;/sub&gt;</td>
<td>Bulk density</td>
</tr>
<tr>
<td>θ</td>
<td>Aquifer porosity</td>
</tr>
<tr>
<td>K&lt;sub&gt;d&lt;/sub&gt;</td>
<td>Distribution coefficient</td>
</tr>
<tr>
<td>M</td>
<td>Aqueous phase concentration of biomass</td>
</tr>
<tr>
<td>S</td>
<td>Aqueous phase concentration of substrate</td>
</tr>
<tr>
<td>A</td>
<td>Aqueous phase concentration of electron acceptor</td>
</tr>
<tr>
<td>μ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Bacterial maximum specific growth rate</td>
</tr>
<tr>
<td>K&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Substrate half saturation constant</td>
</tr>
<tr>
<td>K&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Electron acceptor half saturation constant</td>
</tr>
<tr>
<td>B</td>
<td>Endogenous bacterial decay rate</td>
</tr>
<tr>
<td>k</td>
<td>Rate constant</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>λ</td>
<td>First order decay rate</td>
</tr>
<tr>
<td>v&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Retarded contaminant velocity</td>
</tr>
<tr>
<td>b</td>
<td>Thickness of aquifer</td>
</tr>
<tr>
<td>L</td>
<td>Plume length</td>
</tr>
<tr>
<td>W</td>
<td>Plume width</td>
</tr>
<tr>
<td>v&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Average pore water velocity</td>
</tr>
<tr>
<td>Q&lt;sub&gt;bio&lt;/sub&gt;</td>
<td>Biodegradation sink term</td>
</tr>
<tr>
<td>χ&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Utilization rate of electron donor</td>
</tr>
<tr>
<td>χ&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Utilization rate of electron acceptor</td>
</tr>
<tr>
<td>Y&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Bacterial yield coefficient of electron donor</td>
</tr>
<tr>
<td>Y&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Bacterial yield coefficient of electron acceptor</td>
</tr>
<tr>
<td>M&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Initial biomass concentration</td>
</tr>
<tr>
<td>m</td>
<td>Contaminant mass</td>
</tr>
<tr>
<td>m&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Contaminant mass in the base case</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION
Chapter 1

Introduction

1.1 Background

Groundwater contamination with petroleum hydrocarbons is one of the most serious problems that deteriorate groundwater quality. Nonaqueous phase liquids (NAPLs) are multicomponent organic mixtures that have different water solubility when contact with water. NAPLs are classified into two groups. The liquids in the first group have a density less than the water density and are called light NAPLs (LNAPLs) such as fuel hydrocarbons including gasoline and benzene. The liquids in the second group have density higher than the water density and are called dense NAPLs (DNAPLs) such as chlorinated solvent, PCBs and PAHs. Some of the light NAPLs dissolve in the water in the pores when introduced into the vadose zone, others may exist in the gas phase in the pores or adsorb onto aquifer materials. LNAPLs may not dissolve in unsaturated zone and reach the saturated zone forming a floated layer above the water table. When DNAPLs reach the water table, they continue their descending movement until they reach an impermeable layer as shown in Figure 1.1. Some of DNAPLs could form globules that trap in the pores and become hard to remove. DNAPLs remain on the aquifer bed and dissolve slowly into the moving groundwater which may take hundreds of years or even more (Masters, 1997).

PAHs are polycyclic aromatic hydrocarbons which are composed of two or more benzene rings. They are considered to be the main composition of petroleum and its byproducts. The soluble aromatic hydrocarbons could penetrate the vadose zone and reach groundwater through leakage from underground storage tanks and pipes connections or valves. An attempt to overcome this problem by replacing steel tanks by fiber glass tanks failed because leakage may still occur due to faulty piping (Bedient et al., 1990). The biodegradation process is the transformation of complex compounds into secondary...
substrates by the act of microbial catalyst. It may occur at the leakage area or during the movement of contaminants in the subsurface. The biodegradation of PAHs relies on the contaminant chemical structure and the enzymatic conditions. Before degradation process starts, an acclimatization period normally occurs in which no degradation takes place. Its duration ranges from less than one hour to several months depending on the complexity of the contaminant structure and concentration, and also on the biochemical conditions in the subsurface (Suthersan, 1997).

The degradation reactions of the contaminant should be identified before choosing bioremediation as a treatment technique. This requires the determination of the "metabolism modes" either aerobic or anaerobic. In the aerobic mode, oxygen acts as electron acceptor which is known as "aerobic respiration". In anaerobic mode oxygen is not available. Three kinds of reactions under anaerobic conditions may take place including, anaerobic respiration, fermentation and methane fermentation. In anaerobic respiration, oxidized inorganic or organic compounds act as electron acceptor and the end products are carbon dioxide and water. In the fermentation process, organic compounds act as electron acceptor and electron donor. In the methane fermentation, the substrate is
subjected to oxidation-reduction reaction; therefore the end products are carbon dioxide and methane as gases and organic compounds such as acids and alcohols.

The structure biodegradability relationship affects the degradation of PAHs under aerobic and anaerobic conditions. Degradation of PAHs is influenced by six factors, the solubility of PAHs, the number of fused rings, substitution types, numbers, positions and nature of atoms in heterocyclic compound.

The cometabolism is the transformation process of contaminants, when they become secondary substrate for the growth of bacteria. If the biotransformation removes the toxicity of contaminants, it is called 'detoxification'. In the detoxification process the toxic substance becomes inactive. Detoxification includes several processes namely, hydrolysis, hydroxylation, dechlorination and demethylation. The products from cometabolism process done by one organism can be the energy source for another organism.

Remediation is a process by which the movement and/or the toxicity of certain contaminants is reduced or removed at a specific site. Selecting appropriate remediation techniques should be based on the contaminant type, the hydrogeologic characteristic of the site and the contaminant source in the subsurface.

One of the most important hydrogeologic parameters is the hydraulic conductivity, K, (or the transmissivity, T). Hydraulic conductivity shows how easy is the transportation of water, contaminants, nutrients, NAPLs and air or vapor. Figure 1.1 illustrates the distribution of DNAPL, dense vapor and dissolved chemical plume in the subsurface. For effective bioremediation, the hydraulic conductivity of the subsurface is preferable to be higher than $10^{-4}$ cm/sec and abundant of microorganism is also required (Bedient et al., 1990).
In bioremediation technique, microorganisms are used for the degradation of organic contaminants in unsaturated or saturated soil. This technique has an advantage over the others that it is in situ treatment; i.e. "treat the problem rather than moving it to somewhere else". It is considered to be a natural treatment process and a "cost effective" method (Charbeneau et al., 1992).

There are some factors that cause biodegradation and bioremediation to cease such as the concentration of contaminant which may be toxic to the microorganism, microorganism density, the value of pH of the liquid phase (water), the moisture content of the site of concern as well as the availability of nutrients and electron acceptors.

Several site specific factors affect the microbial population, biodegradation rates and the contaminant fate. These factors could be classified into microbial, nutrients and physical-chemical factor. In soils, there are five major different microbial populations; including, bacteria, actinomycetes, fungi, algae and protozoa. Bacteria are normally present in large amounts and are characterized by high rate of growth and ability to degrade different kinds of contaminants (Suthersan, 1997).

Bacteria might be classified according to: availability of oxygen, cell structure and the type of energy and carbon source. In term of oxygen availability, bacteria are categorized into three groups; aerobic when oxygen is present, anaerobic when oxygen is absent, and facultative in both situations. Bacteria’s cell could be in rod shape which could be present in large amount, in spherical shape, or in spiral shape which are uncommon in soils. Based on energy type and carbon source, bacteria could be classified into heterotrophic and autotrophic. Heterotrophic use the organics as energy and carbon source, while the autotrophic use the sunlight as energy source or obtain it from the oxidation of inorganic compounds and use carbon dioxide for the carbon source (Suthersan, 1997).
The microbial living cell consists mainly of carbon; 95% by weight are carbon, hydrogen, oxygen and nitrogen and 70% of the rest are phosphorus and calcium. The bacteria has chemical structure of \( \text{C}_{5}\text{H}_{70}\text{N} \). Carbon is provided from organic contaminant or inorganic source as carbonate or bicarbonate, water supplies O and H, whereas the other trace nutrients are present in soils and aquifers. When one of these trace nutrients become deficient, it is called limiting factor as expressed by Liebig’s Law of the minimum:” The essential constituent that is present in the smallest quantity relative to the nutritional requirement of microorganisms will become the limiting factor of growth.” (Suthersan, 1997).

The physical-chemical factors are divided into four elements; temperature, pH, moisture content, and the redox potential. Arhenius behavior for the chemical-biochemical reactions rate is illustrated in Figure 1.2. It increases as the temperature increases to certain extent. Temperature dependency (Figure 1.3) shows how temperature affects the growth rate of different microorganisms. Psychrophiles have optimum temperature at \( 15\pm5^\circ\text{C} \) and minimum at \( 0^\circ\text{C} \) or below, while Mesophiles have optimum temperature ranges from \( 10^\circ\text{C} \) up to \( 40^\circ\text{C} \) and they are resident in the subsurface. Therophiles have optimum temperature above \( 45^\circ\text{C} \). The value of pH affects the function of the cells of the microorganisms, the transportation of the cell membrane and the catalyst reactions equilibrium. The natural environment has a value of pH between 5 and 9. However, a pH value between 6 and 7.5 is preferred. Acidophilic bacteria function near a pH value of 2.5, while alkalophilic bacteria function at a pH range from 10 up to 12. The moisture content factor plays a vital role in the bioremediation process; it affects the bioavailability of contaminant, the gas transfer, the toxic level of contaminant, the growth of microorganism, and movement and distribution of the species. Also the redox potential which gives an idea about the chemical conditions of the environment of concern in term of oxidation-reduction reactions, affects
Figure 1.2: The relation between microbial activity and temperature (Source: Suthersan, 1997).

Figure 1.3: Temperature dependency of growth rate of various microorganisms (Source: Suthersan 1997).
the microorganism metabolism and the activity of the enzyme. Redox potential is denoted by $E_{Hi}$. If $E_{Hi}$ is higher than zero, then oxidizing condition is prevailed, whereas reducing condition is prevailed when $E_{Hi}$ is lower than zero. Naturally, the environment has redox potential of -400 mV and up to +800 mV.

1.2 Transport Process in the Subsurface

The transport of the hydrocarbon contaminant in groundwater systems is governed by different physical, chemical and biological processes such as diffusion, advection, dispersion, adsorption, volatilization and biodegradation. Volatilization is the transformation of the chemical from the aqueous phase into the gas phase. This process is insignificant when compared to other processes; the organic vapor depleted from the subsurface especially in the shallow water table case over the time. The expected contaminant mass loss due to volatilization is lower in the case of less volatile hydrocarbons (Parcher, 1999).

Dissolved solutes in the subsurface transport from high concentration areas to the low concentration areas. This kind of the transport, which requires gradient in the concentration, is called diffusion. However, the diffusion process is more complicated in the case of the adsorbed solute which makes the diffusion process slow. Fick’s first law explains the relation between the solute diffusing in one dimension and the gradient in the concentration as follow:

$$F = -D_d \left( \frac{dC}{dx} \right)$$

(1.1)

where $F$ is flux of solute per unit area per unit time, $D_d$ is the diffusion coefficient ($L^2/T$), $C$ is the solute concentration ($M/L^3$) and $dC/dx$ is the concentration gradient ($M/L^3/L$). The negative sign indicates that the direction of the solute movement is from the higher concentration area to the lower concentration one. The diffusion coefficient changes with the temperature, but does not depend on the solute concentration.
When solute concentrations in one dimension vary with time, Fick's second law is given as:

$$\frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial x^2}$$  \hspace{1cm} (1.2)

where $\frac{\partial C}{\partial t}$ is the change of solute concentration with respect to time (M/L$^3$/T).

It is observed that the transport of solute in porous media takes long pathway and becomes slower than that in plume. Therefore, an effective diffusion coefficient should be considered; $D^* (L^2 T^{-1}),$

$$D^* = \omega D_d$$  \hspace{1cm} (1.3)

where $\omega$ is tortuosity coefficient which considers the pathway shape in the porous media that water follows through. The tortuosity coefficient is always greater than one. When the water flows around sediments, a diversion of its path occurs. It will be shorter in the case of well sorted sediment and larger in poor sorted sediment.

The dissolved solutes in the subsurface move with the flowing water in a process called advection or convection. The average rate of the movement of water in the subsurface in one dimension is higher than the average linear velocity ($v_x$) which is the rate of water flux through a unit cross sectional area in the porous media where the tortuosity is considered and the flow occurs through the effective porosity. The average linear velocity is given as:

$$v_x = \left( \frac{K}{n_e} \right) \left( \frac{dh}{dl} \right)$$  \hspace{1cm} (1.4)

where $v_x$ is the average linear velocity (L/T), $K$ is the hydraulic conductivity (L/T), $n_e$ is the effective porosity (1) and $dh/dl$ is the hydraulic gradient (L/L).

The flux of solute in one dimension due to advection can be calculated as:

$$F_x = v_x n_e C$$  \hspace{1cm} (1.5)

The advective transport in one dimension is given as:
\[ \frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} \]  

(1.6)

The site heterogeneity plays important role in the movement of dissolved solutes in the subsurface as it affects the spreading of the solute.

At the macroscopic scale, where large scale of volume that influence single pores is considered, the groundwater moves faster in the centre of pores than in its edges. Also, some of water particles will take a longer path and others will follow a linear path, and when large pores occur, the flow of water becomes faster.

When groundwater with dissolved solutes moves at different rates; mixing happens. Such process is called mechanical dispersion and it results in the dilution of solutes at the advancing edge of flow. Longitudinal dispersion happens along the flow path direction; whereas transverse dispersion happens in the normal direction of the flow path. Both can be described by the following equations:

longitudinal mechanical dispersion coefficient = \( \alpha_i v_i \)  

(1.7)

transverse mechanical dispersion coefficient = \( \alpha_j v_i \)  

(1.8)

where \( v_i \) is the average linear velocity in \( i \) direction (L/T) and \( \alpha_i \) and \( \alpha_j \) are dynamic dispersivities in \( i \) and \( j \) directions (L), respectively.

The diffusion process is linked to the mechanical dispersion process in groundwater and the combination of these two processes is called hydrodynamic dispersion process. The hydrodynamic dispersion coefficient, \( D_i \), is defined as follows:

\[ D_i = \alpha_i v_i + D^* \]  

(1.9)

\[ D_T = \alpha_T v_i + D^* \]  

(1.10)

where \( D_L \) and \( D_T \) are longitudinal and transverse hydrodynamic dispersion coefficients (L²/T), respectively, and \( \alpha_L \) and \( \alpha_T \) are longitudinal and transverse dynamic dispersivities (L), respectively.
When the dissolved solute sorbed onto the surface of the aquifer materials, a slow solute movement will result in comparison to the groundwater movement causing what is called retardation. The sorption process includes adsorption, chemisorption, absorption and ion exchange. Adsorption occurs when the solute is held tightly to the solid surface, while the cation exchange is encountered when the cation is attached to clay mineral surface that has negative charge. Chemisorption occurs when the chemical reaction between solute and solid surface happens, while absorption is due to diffusion of the solute into the interior surface of the porous particle.

The direct relationship between the mass of the sorbed solute and its concentration can be described by a linear sorption isotherm as follows:

\[ C' = K_d C \]  

(1.11)

where \( C' \) is the solute mass sorbed per unit dry weight of the solid (MM\(^{-1}\)), \( C \) is the solute concentration (ML\(^{-3}\)) and \( K_d \) is the distribution coefficient (L\(^3\)M\(^{-1}\)).

The retardation factor could be calculated from the following relation:

\[ R = 1 + (\frac{\rho_b}{\theta})K_d \]  

(1.12)

where \( R \) is the retardation factor (dimensionless), \( \rho_b \) is the bulk density (ML\(^{-3}\)) and \( \theta \) is the porosity for saturated media (dimensionless).

Another sorption isotherm is the Freundlich which describes the non linear relationship between the mass of the sorbed solute and its concentration:

\[ C' = KC^N \]  

(1.13)

where \( K \) and \( N \) are dimensionless constants.

In the biodegradation process, the contaminant is consumed by the microorganism through redox reactions. The biodegradation of the contaminant under aerobic condition, when oxygen is used as electron acceptor, can be expressed by the modified Monod
function. The equation of the microbial growth due to the contaminant removal is described as:

\[
\frac{dM}{dt} = \mu_{\text{max}} M \left( \frac{S}{K_s + S} \left( \frac{A}{K_a + A} \right) \right) - BM
\]

(1.14)

where \( S \) is the aqueous substrate (electron donor) concentration (ML\(^{-3}\)), \( A \) is the aqueous phase electron acceptor (oxygen) concentration (ML\(^{-3}\)), \( M \) is aqueous phase concentration of biomass (ML\(^{-3}\)), \( \mu_{\text{max}} \) is the bacterial maximum specific growth rate (T\(^{-1}\)), \( K_s \) is the substrate half saturation coefficient (ML\(^{-3}\)), \( K_a \) is the electron acceptor (oxygen) half saturation coefficient (ML\(^{-3}\)), and \( B \) is the endogenous bacterial decay rate coefficient (T\(^{-1}\)).

### 1.3 Remediation Techniques

When a contaminated site undergoes remediation process, two important factors should be considered, the possibility of soluble contamination plume to migrate off site and the location of the contaminant source. A study conducted by EPA in 1989 to evaluate twenty two different groundwater remediation systems indicated that the mass of the hydrocarbons contaminant decreased significantly. However, the rate of the decrease in concentration of the contamination was slower than expected.

There are many factors that affect groundwater remediation. The contaminant related factors include the presence of NAPLs, highly sorbed contaminant and the continuous leaking from the contaminant source; hydrogeological factors and design factors. The hydrogeological factors include the heterogeneity of the site, the low permeability and the existence of fractures. The design factors include the rate of the pumping and the locations of the recovery wells (Bedient et al., 1990).

The main goals of groundwater remediation systems are to control the soluble migration of contaminant plume off site, stop the leaking from the contamination source, and treat the contaminated water to be suitable for drinking purpose. The pump and treat system shows a good performance in controlling off site or at site boundary.
function. The equation of the microbial growth due to the contaminant removal is described as:

\[
\frac{dM}{dt} = \mu_{\text{max}}M \left( \frac{S}{K_s + S} \right) \left( \frac{A}{K_a + A} \right) - BM
\]

where \( S \) is the aqueous substrate (electron donor) concentration (ML\(^{-1}\)), \( A \) is the aqueous phase electron acceptor (oxygen) concentration (ML\(^{-1}\)), \( M \) is aqueous phase concentration of biomass (ML\(^{-3}\)), \( \mu_{\text{max}} \) is the bacterial maximum specific growth rate (T\(^{-1}\)), \( K_s \) is the substrate half saturation coefficient (ML\(^{-1}\)), \( K_a \) is the electron acceptor (oxygen) half saturation coefficient (ML\(^{-3}\)), \( B \) is the endogenous bacterial decay rate coefficient (T\(^{-1}\)).

### 1.3 Remediation Techniques

When a contaminated site undergoes remediation process, two important factors should be considered, the possibility of soluble contamination plume to migrate off site and the location of the contaminant source. A study conducted by EPA in 1989 to evaluate twenty two different groundwater remediation systems indicated that the mass of the hydrocarbons contaminant decreased significantly. However, the rate of the decrease in concentration of the contamination was slower than expected.

There are many factors that affect groundwater remediation. The contaminant related factors include the presence of NAPLs, highly sorbed contaminant and the continuous leaking from the contaminant source; hydrogeological factors and design factors. The hydrogeological factors include the heterogeneity of the site, the low permeability and the existence of fractures. The design factors include the rate of the pumping and the locations of the recovery wells (Bedient et al., 1990).

The main goals of groundwater remediation systems are to control the soluble migration of contaminant plume off site, stop the leaking from the contamination source, and treat the contaminated water to be suitable for drinking purpose. The pump and treat system shows a good performance in controlling off site or at site boundary.
The most accepted strategies for the contaminant remediation in subsurface layers include complete removal of the source such as excavation, controlling contaminant source by barriers or hydraulic control, and finally reducing the contaminant mass by bioremediation, soil vapor extraction and natural attenuation (Bedient et al., 1990).

There are many conventional remediation methods and new technologies available for groundwater remediation. A combination between chemical technologies, biological methods and physical technologies (Appendix A) can be powerful to remove contaminant from source zone or reduce the contamination in groundwater. Table 1.1 presents advantages and disadvantages of physical techniques.

1.3.1 Chemical Technologies

Chemical Oxidation

In situ chemical oxidation technique is based on adding oxidant reagent through the injection wells into soil and/or groundwater as clarified in Figure 1.4. The most popular oxidant reagents are hydrogen peroxide-based Fenton’s reagent, and potassium permanganate while ozone is non common oxidant reagent.

Fenton’s reagent could be produced on site by adding iron catalyst to hydrogen peroxide solution, however this reagent works perfectly in acidic condition; therefore pH should be adjusted. Also potassium permanganate solution could be prepared on site using potassium permanganate crystals (Motsch et al., 2002). The Persulfate is also very strong oxidant that is widely used in industrial processes and commercial products as chemical destruction of organic contaminant such as BTEX, MTBE, chlorinated solvents and PCBS from soil and water. However, heat, metal ions (e.g. Fe$^{2+}$) or another catalyst are needed to achieve oxidation (Alliance Remediation Solution Inc., 2007).
<table>
<thead>
<tr>
<th>Technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2. Installation caused few disturbances in the operation site.</td>
<td>2. Uncontrolled movement of dangerous vapor can occur.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. No treatment required above surface.</td>
<td>3. Not suitable for stratified soil.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4. Effective in treating VOC.</td>
<td>4. Deep injection required high pressure and, therefore high cost.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. Few disturbances in water table elevation and small smear zone in created.</td>
<td>2. Low vacuum efficiency in high permeable soil.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. Suitable for deep groundwater.</td>
<td>3. Mixing between phases can occur if removed in one stream.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4. LNAPL trapped in pores are down over groundwater.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dynamic Underground Stripping with Hydrous Pyrolysis Oxidation</td>
<td>1. No treatment required above surface.</td>
<td>1. Small particles and decayed microorganisms can clog the system.</td>
<td>Motsch et al. (2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. High consumption of energy.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. DNAPL migration can occur.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4. Treated soil can remain at high temperature for long time after treatment.</td>
<td></td>
</tr>
<tr>
<td>Skimming</td>
<td>1. Little discharge of water.</td>
<td>1. Low rate of recovery.</td>
<td>Motsch et al. (2002)</td>
</tr>
<tr>
<td></td>
<td>2. Thin layer of LNAPL can be recovered.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2. Used in high depth, 91 m.</td>
<td>2. Can raise groundwater level and dissolve contaminant.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Not suitable for saturated zone.</td>
<td></td>
</tr>
</tbody>
</table>
Table 1.1: Advantages and disadvantages of physical techniques (Cont.)

<table>
<thead>
<tr>
<th>Physical technique</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeable reactive barrier</td>
<td>1. No pumping, reduce operation and maintenance costs.</td>
<td>1. No stability for wall materials over time is assured.</td>
<td>Puls et al. (1998)</td>
</tr>
<tr>
<td></td>
<td>2. Sites can be used during cleanup.</td>
<td>2. Funnel and gate PRB affect groundwater velocity.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3. No energy consumed.</td>
<td>3. Contamination should not be deeper than 15 m.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4. No structures required above surface.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Pumping and extraction system are required.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. High cost.</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.4: Chemical oxidation technique (Source: Motsch et al., 2002).
1.3.2 Biological Technologies

Bioremediation

Microorganisms can degrade petroleum hydrocarbons in the subsurface, under certain conditions, and produce carbon dioxide and water as end products. Bioremediation has advantage over other techniques that the destruction of the contaminant results in less harmful end products. Under the proper conditions, this process could occur without the influence of human beings which is called intrinsic bioremediation or natural attenuation. In this case, site monitoring is required to follow up any deficiency in nutrients or electron acceptors. Additionally, bioremediation is less expensive and can be powerful in removing contaminants that are sorbed to aquifer materials or dissolved into groundwater. Furthermore, it can work where construction facilities hinder the use of other techniques.

Two important points should be considered before choosing bioremediation as a technique to remove contaminant. The first point is related to the hydrogeological conditions of the subsurface. High hydraulic conductivity is required, so that the nutrients and electron acceptor can transport easily through the aquifer. The second point is that presence of microorganisms should be assured. Laboratory experiments, simulating the transport and delivery of nutrients, should be conducted to assess the technique’s efficiency.

Before starting bioremediation in a contaminated site, it should be confirmed that microorganisms present in the site are capable of degrading the contaminant. Soil analysis could give information about nutrients availability in the site, however, groundwater analysis could indicate further nutrients requirement in the site. For instance, the existence of silt and clay layer increases the nutrient sorption properties of the aquifer materials and therefore increases the required amount of nutrients needed for the bioremediation process to proceed.
Bioventing

Bioventing is an effective system in simulating the natural biodegradation aerobically in the soil. The system consists of injection wells and air blowers. The injecting wells are to introduce the nutrients, air and moisture to induce the bioremediation process (Figure 1.5). However, bioventing is effective in the bioremediation of ground water at a depth of 3 m (Motsch et al., 2002).

Enhanced Bioremediation

The enhancement of the bioremediation process requires the addition of microorganisms such as fungi and supplying nutrient and air. The nutrients are introduced to the subsurface though injection wells, Figure 1.6. There is an alternative way for pumping oxygen which is the injection of diluted hydrogen peroxide solution. It is effective in removing its extra oxygen atom and form water and free oxygen. Furthermore, adding nitrate solution as additional electron acceptor in the contamination zone can accelerate the biodegradation process. Also, the addition of suitable microorganisms to the soil will increase the biodegradation rate (Motsch et al., 2002).

Phytoremediation

In phytoremediation process, plants are used for removing, transforming, stabilizing and or destroying organic and inorganic contaminants. It is effective in the soil remediation within 1.0 m and in groundwater remediation to a depth of 3 m. The plants in certain cases should be treated as waste. phytoremediation process includes four steps; enhancing rhizosphere biodegradation, phyto-extraction/ phyto-accumulation, phyto-degradation and phyto-stabilization. There is natural substance released by the plant roots, it supplies the nutrient to the microorganisms. This is known as enhanced rhizosphere biodegradation.

Phyto-extraction/ phyto-accumulation is the process of up-taking the contaminant
Figure 1.5: Bioventing system (Source: Motsch et al., 2002).

Figure 1.6: Enhanced bioremediation (Source: Motsch et al., 2002).
by plant roots to the plant leaves and shoot. The third step is phyto-degradation in which contaminant metabolism process by the plant tissues. The contaminant immobilization at the interface between soil and roots is the forth step which is defined as phyto-stabilization (Motsch et al., 2002).

1.4 Scope and Objectives

Since 1900s different chemical wastes have been generated as a result of developments in industrial fields that serve human needs. Most of these chemicals represent potential threat to the groundwater quality. Many organic and inorganic chemicals are recognized as contaminant sources for the groundwater. Different trace metals, nitrates and brine are examples of inorganic contaminants, while synthetic organic chemicals such as chlorinated solvents, pesticides and fuels are examples of organic contaminants.

The most common organic contaminants in groundwater could be categorized into groups: including, fuel and derivatives; benzene, toluene, ethylbenzene and xylene (BTEX), polycyclic aromatic hydrocarbons (PAHs), alcohols and ketones, halogenated aliphatics (trichloroethylene), halogenated aromatics (chlorobenzene), and polychlorinated biphenyls (PCBs). Normally, halogenated hydrocarbons are associated with DNAPL releasing.

The nonaqueous phase liquids (NAPLs) are organics that exist as separate phase when coming into contact with water. The differences in the physical and chemical properties between NAPLs and water lead to the formation of immiscible layer and make the process of water restoration difficult. NAPLs are composed of either single chemical or complex mixture of chemicals. BTEX compounds are typically associated with LNAPL releasing.
The improper way of disposing petroleum byproduct into the surface may cause contamination in both saturated and unsaturated zones as separate phases due to their solubility. When surface water infiltrates into subsurface, groundwater flows through the entrapped NAPL; partial dissolution of NAPLs occurs and results in the formation of the dissolved contaminant plume downstream of the source zone. Most of the research regarding this problem focused on removing the source mass (NAPL) or treating the contaminant plume to reduce its concentration to a safe level.

The release of nonaqueous phase liquids (NAPLs) to groundwater systems in petroleum oil fields is a serious and widespread problem. Bu Hasa is the first GASCO Natural Gas Liquid Extraction Plant in UAE and was commissioned in 1981. It processes associated gas from the neighboring Bu Hasa oil field operated by ADCO in the central desert. It is located 50 km from Habshan – Bab Gas Complex and 175 km from Abu Dhabi city. It extracts natural gas liquid (NGL) from rich sour gas and delivers lean gas to ADCO gas injection compressor. The extracted NGL is transported to Ruwais along with NGL from the other sites to the GASCO NGL fractionation plant, to produce C2 (Ethane), C3 (Propane), C4 (Butane) and C5+ (Pentane plus).

Since 1999, GASCO contracted different companies to assess groundwater quality and to identify the possible contamination of the aquifer. In 2000, hydrocarbon contamination in the Liwa aquifer, in the vicinity of former warm blowdown area in Bu Hasa LRP, was detected (URS Corporation, 2006). Currently, URS Corporation is carrying out a remediation project in this area.

In this thesis, the numerical model MITABIOTRANS (Mohamed, 2001, Mohamed et al., 2006, Mohamed et al., 2007) is used to assess the fate and transport of the dissolved hydrocarbon plume in Liwa aquifer originated from the residual free phase contaminant in Bu Hasa LRP. The main goal of this thesis is to assess the extent of contamination and
develop a strategy to minimize the concentration of dissolved contaminant reaching the production wells in the camp area downstream of the source of contamination. Towards that goal, and due to the absence of accurate data, sensitivity analysis will be performed to study the effect of several controlling physical and biological parameters on the natural attenuation of the plume. Based on such an analysis, the degradation process can be enhanced by improving the conditions leading to thriving bacterial activities. In addition, more efforts should be placed on data collection regarding parameters that have more influence on the degradation of the product. Several bioremediation scenarios will be evaluated in order to select the best one that satisfies the main goal of this study.

1.5 Organization and Contents

The thesis is composed of seven chapters. Chapter one presents terminologies related to the biodegradation process including reaction modes and physical, chemical and biological site factors that affect biodegradation. It also reviews the transport processes in groundwater systems such as advection, diffusion and adsorption. A description of the common remediation technologies of groundwater contamination with NAPLs such as physical and biological are included. Some of the latest studies that focused on groundwater contamination with NAPLs are presented in Chapter two. A review of the kinetic expressions for modeling biodegradation such as Monod and instantaneous reaction and previous studies that used common numerical models in the simulation of the biodegradation is presented. Chapter three is devoted to the description of Bu Hasa site, the contamination incident and the natural gas processing in Bu Hasa LRP. Chapter four presents a brief description of METABIOTRANS, that is used in this thesis and the governing equations that describe the transport processes of the electron acceptor and the electron donor in the subsurface. It discusses the hydrological information and the lithology of Liwa aquifer, as well as the model parameters. Chapter five presents a
sensitivity study of the expected dissolved plume migration to several parameters such as
the maximum specific growth rate, bacterial decay rate, half saturation constant, microbial
yield coefficient, flux and dispersivity. In Chapter six, the model is used to simulate
several remediation scenarios in order to assess their effects on contaminant migration to
the production wells in the camp area. Summary and conclusions of the work are presented
in Chapter seven. A list of references is included at the end of this thesis.

1.6 Limitations

Numerical models simulate physical systems such as groundwater systems, but
several limitations are inherent in any numerical model. The model used in this thesis is
useful in predicting the dissolved plume migration under several flexible conditions,
however limitations do exist. These limitations include data availability and model
limitations. For example, the model considers attached biomass and does not consider
biomass transport. Also, although the model can simulate heterogeneous aquifer, it was not
considered in the thesis. A simplified homogenous aquifer was assumed. Another
assumption is that only benzene plume is considered and no chemical reaction between
different contaminants that may exist in the aquifer is assumed.
CHAPTER 2

LITERATURE REVIEW
Chapter 2

Literature Review

2.1 Mathematical and Numerical Modeling of Hydrocarbon Biodegradation

About two millions of underground storage tanks out of ten millions in the U.S are used for storing gasoline (Zhang et al., 1995). Leakage problems associated with corrosion and fractures result in groundwater contamination with petroleum hydrocarbons. Therefore, remediation of the contaminated sites is required (Zhang et al., 1995).

Molz et al. (1986) and Widdowson et al. (1987) developed aerobic biodegradation models for organic contaminants considering one and two dimensions and advective and dispersive processes which were known as microcolony models. In this model, the bacteria microcolonies were assumed as disks that had similar radius and thickness attached to aquifer materials. It was also assumed that the substrate and the oxygen were diffused to the bacteria colonies through aquifer boundaries.

The model’s observations demonstrated that the biodegradation process played an effective role in the contaminant transports under suitable growth conditions. The results of the 2-D model indicated that biodegradation under aerobic condition caused a reduction in the substrate concentration in the longitudinal direction of the plume and retardation was observed. However, in the plume centre, anaerobic condition prevailed due to the lack of the oxygen and bacteria. In 1988, Widdowson et al. modified their work to include the heterotrophic and facultative bacteria. The metabolism process is affected by the lack of substrate, the electron acceptor; oxygen and/or nitrate and the nutrient, either individually or simultaneously. The oxygen and the substrate transports in the porous medium were controlled by advection, dispersion and adsorption processes (Bedient et al., 1990).

Minsker and Shoemakor (1998), Hunter et al. (1998) l, and Tebes-Stevens et al. (1998) neglected the interaction between the substrates. However, some researchers
considered the substrates interactions such as MacQuarrie (1997) who developed a three dimensional model considering the substrate and the geochemical interactions. Also Zhang et al. (1995) considered the interaction between the attached biomass to the solid phase and the sorbed organic contaminant to soil or aquifer materials and their effect on the biotransformation rate. Minsker and Shoemakor (1998), Hunter et al. (1998) I, and Tebes Stevens et al. (1998) described the advection, dispersion, sorptive retardation and chemical or biological reaction either in 1D, 2D or 3D taking into account the biodegradation process with one substrate or more. (Schirmer, 2000).

Zhang et al. (1995) addressed the biofilm theory as an approach to describe the bioremediation process in the field. They used the biotransformation model (Biofilm Accumulation Model; BAM) in the subsurface which is originated from the mixed culture biofilm model (BIOSIM). It was assumed that the surface is completely surrounded by film to ensure same substrate flux and therefore simplify the mathematical derivations. They performed a batch experiment in order to examine the effect of attached biomass on the biodegradation rate of naphthalene. The biodegradation rate was lower in the presence of soil than in the absence of soil. They discussed the kinetic of biofilm through mass balance equations for the organic compound and the biomass within porous soil medium, biofilm and bulk liquid phase. It was concluded that biotransformation rates of strongly hydrophobic compounds such as polyaromatic hydrocarbons, are affected by the bioavailability of microorganisms. The biostimulation process by which all suitable conditions for growing microbes are supplied was powerful when the biodegradation rate is slower than the desorption rate (Zhang et al., 1995).

Zhang et al. (1995) concluded that supplying nutrients and trace metals had smaller effect on the biotransformation rate of benzene, naphthalene, phenanthrene and pyrene as compared to the effect of increasing the temperature. However, Holliger et al. (1997)
believed that sufficient nutrients in the subsurface are adequate to provide aerobic condition for biodegradation to take place. They concluded that anaerobic biodegradation is preferred due to less production of biomass and the availability of the electron acceptors.

When biodegradation is connected with the transport processes in certain systems, the rate of biodegradation depends on the existence of active microbes and the availability needed for microbial growth. Physical properties such as hydraulic residence time, dispersion–diffusion processes and the site heterogeneity could affect the biodegradation process. If the site is contaminated with DNAPL products such as trichloroethene (TCE) and tetrachloroethene (PCE), DNAPL products could migrate into saturated zone of aquifers very fast causing contamination in the regions which will act as source of contaminant for long time.

Wang et al. (1999) used ParSSim; a parallel simulator of subsurface flow, transport and reaction to illustrate the physical and chemical processes that affect the performance of the intrinsic bioremediation and consequently on the NAPL contaminant concentration trapped in the saturated zone. The NAPL was assumed to be a mixture of trichloroethylene (TCE) and perchloroethylene (PCE). Also, Clement et al. (2004) studied the combined influence of DNAPL dissolution transport process, the sorption process and the biodegradation process on the contaminant mass in saturated porous media using mathematical modeling. LiLi et al. (2001) examined the effect of hydraulic residence time and initial substrate concentrations on the microbial growth and biodegradation by using dimensionless transport model associated with Monod equations. Clement et al. (2004) solved the equations using RT3D; a general purpose reactive transport code. It was assumed that the trapped DNAPL in the subsurface remain stationary and the DNAPL had no effect on porosity and hydraulic conductivity of aquifer. These assumptions are accepted in the case of low saturation level of DNAPL. PCE was selected to represent
DNAPL species because it is a common industrial contaminant. PCE can be biodegraded under anaerobic condition to ethene as follows: \( \text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE (dichloroethene)} \rightarrow \text{VC (vinyl chloride)} \rightarrow \text{ethene} \) (Clement et al., 2004).

Wang et al. (1999) concluded that physical processes such as injection and extraction rate affected the dissolution and biodegradation rates. They also found that the contaminant mass transfer and its attenuation are affected by the dispersion process depending on the flow in the field and the location of the contaminant source. They observed that the high dissolution rate can hinder the activity of the microbes earlier. On the other hand, low dissolution rate combined with the biodegradation process gave optimistic predication of the time required for the treatment; the existence of low NAPL concentration in the downstream in spite of the remaining of large contaminant mass.

Clement et al. (2004) concluded that area close to DNAPL source is contaminated with PCE, while "daughter products" were distributed over wider areas. However, VC profile was wider than DCE, thus monitoring the bioremediation is required to avoid the accumulation of toxic compound such as VC. It is also observed that when high biodegradation rate for PCE was applied, high reduction in PCE and TCE was observed, while the concentrations of DCE and VC were high. The concentration of aqueous phase was lower when the degradation rate was assumed to occur in solid and liquid phases. This may happen as a result of the consumption of the contaminant mass on solid phase leading to the decrease of the contaminant concentration in the solid phase (Clement et al., 2004).

LiLi et al (2001) considered two situations. In the first case, the bacteria transport and the existence of byproducts that inhibit biodegradation was considered, while in the second case, inhibition was ignored. They modeled benzoate and salicylate ignoring sorption and assuming oxygen acts as an electron acceptor. They concluded that at fixed pore-water velocity, the maximum growth rate coefficient is inversely proportional to the
initial substrate concentration. A fixed initial substrate concentration, maximum growth rate coefficient is directly proportional to the pore-water velocity and inversely proportional to residence time. They claimed that the cell transfer and the existence of the inhibitory byproducts could affect the modeled benzoate.

The complete mass removal of DNAPL is unlikely to happen. Mayer and Endres (2007) conducted a study to build up a framework to assess source removal and plume remediation at the same time. To achieve their goals, they assumed physical DNAPL source heterogeneity. Therefore, the rate of contaminant mass release into the plume and the efficiency of the efforts for the source removal are governed by the degree of heterogeneity. In their study they assumed high and low capital and operating costs for using source removal techniques (chemical flushing removal), because it is site dependent.

The framework was helpful in the decision making for the source removal technique and the implementation of plume remediation. Mayer and Endres considered pump and treat methods (PAT) as plume remediation technique and flushing with chlorinated solvent for source removal. The distribution of the funds to source removal or plume remediation was highly affected to the unit costs related to the technique of the remediation. When low cost of chemical flushing was assumed, it was found that the distribution of funds to source removal or plume remediation was highly affected by the source heterogeneity. When they change the time required for a period between the source removal and the implementation of the remediation, the process become effective for the partial removal of source coupled with the plume remediation except for longer time.

Molsen, 2000 developed BIONAPL: a three dimensional model used to assess the efficiency of humic acid as natural organic carrier in enhancing the dissolution and the biodegradation of the residual diesel fuel in groundwater. While Huang et al. (2006) simulated an enhanced in situ biodegradation (EISB) process coupled with three
dimensional multiphase multicomponent (3DMM) contaminant flow and transport by developing numerical and physical models. Huang et al (2006) designed a pilot-scale physical model and used its results for modeling purposes. Dissolved non aqueous phase liquid (NAPLs) was used as contaminant and the biodegradation was simulated under aerobic condition. The model was powerful in simulating EISB process in homogenous and non fracture medium and under equilibrium temperature. The difference in the results was small when compared to the results obtained from the physical model.

Molsen (2000) studied the effect of ethanol as gasoline fuel additive in the persisting of BTEX compounds in groundwater contaminated with gasoline. Also, Chen et al. (2008) studied the effect of the ethanol on the biodegradation of BTEX under anaerobic conditions. Chen et al. (2008) conducted a microcosm experiment using aquifer materials and groundwater collected from Canadian Force Base Borden. Molsen (2000) concluded that the humic acid is effective in decreasing the time required for the complete dissolution of the contaminant diesel source to the fifth. His finding was verified quantitively by carrying out a pilot scale experiment. Molsen also carried out a sensitivity analysis to study the effect of ethanol in the persisting of benzene in gasoline contaminated groundwater. The results showed that ethanol has low influence on the persistence of benzene; a present of 10% ethanol can increase the persistence of benzene by up to 150% after twenty years, where the persistence of benzene is determined by the distance travelled by benzene with concentration of 10 ppb. He found that increasing the persistence of benzene in the presence of ethanol was due to the limitation of the electron acceptor and biodegradation competition.

Chen et al. (2008) developed first an experiment to study the biodegradation of aromatic hydrocarbons in the absence of ethanol. They concluded that natural attenuation occurred and resulted in the degradation of all BTEX and trimethylbenzene (TMB) isomers
under the combined conditions of nitrate and ferric iron. They found that benzene and o-xylene biodegraded under ferric iron condition, but only after the biodegradation of toluene, ethylbenzene and m/p-xylene under denitrification condition. Also, the results showed that 1,2,3-TMB or 1,2,4-TMB biodegraded slowly under iron reducing condition. However, the biodegradation of 1,3,5-TMB occurred first under denitrification condition then under ferric iron condition.

In the second stage, Chen et al. studied the effect of ethanol addition on the biodegradation of aromatic hydrocarbons with and without adding electron acceptors. In the case of using 500 mg/l ethanol without adding electron acceptors, they noticed a quick decline in the concentration of ethanol and its mineralization intermediate (acetate) with a major product of methane. However, slow biodegradation rate of high concentration of ethanol (5000 mg/l) observed under ferric iron condition with the remaining of unidentified volatile fatty acids and low methane concentration. However, the addition of nitrate or ferric iron promoted the bioremediation of ethanol at low and high concentration. The unidentified fatty acids hinder the biodegradation process of BTEX components especially with high ethanol concentration. Denitrification of minor toluene was noticed when low ethanol concentration presented, but after the utilization of ethanol and acetate.

2.2 Laboratory and Field Studies of Hydrocarbons Bioremediation

Parcher (1999) discussed the assessment of the remediation techniques of an aquifer contaminated with the dissolved hydrocarbon from phase separated hydrocarbon using numerical groundwater flow and transport models. Four remedial techniques were considered; natural attenuation, groundwater extraction, groundwater flushing and microbial fence. However, many researches noticed that natural attenuation is effective in reducing the threat of toxic compounds to groundwater quality. Scow and Hicks (2005) agreed that natural attenuation of organic contaminants in groundwater is influenced by
microbial processes that are responsible for contaminant biodegradation and can be enhanced through biostimulation and/or bioaugmentation. Also, Chen et al. (2005) carried out research on two petroleum contaminated sites to evaluate the occurrence of natural attenuation of MTBE (Methyl tert-butyl ether).

Parcher (1999) selected a fuel distribution terminal where the contamination was observed in the unconfined aquifer beneath the terminal and extended off site. She used BIOTRANS model; a two dimensional finite element model that simulates multiple dissolved species in heterogeneous and anisotropic aquifers. She selected benzene and TEX compounds as dissolved species. The effectiveness of the remedial techniques depended on predicted contaminant concentration in the aquifer and the mass removed from the source after twenty years. She concluded that the groundwater flushing showed the best results of benzene and TEX constituents’ mass removal from the source and the reduction in the dissolved species concentration in the aquifer.

Observations of Chen et al. (2005) in two sites indicated the effectiveness of intrinsic biodegradation; depletion of electron acceptors such as dissolved oxygen, nitrate and sulphate; production of dissolved ferrous ion, sulphide, methane and carbon dioxide; increasing in microbial population and the appearance of Tert-butyl alchol (TBA) which is a byproduct of MTBE biodegradation (Chen et al., 2005). Martienssen et al. (2006) depended on the byproducts to trace the natural attenuation of MTBE and concluded that TBA is an indicator for aerobic MTBE biodegradation, however, it required larger reaction zone because of the depletion of oxygen (Martienssen et al., 2006).

In situ bioremediation is one of the remediation techniques of sites contaminated with petroleum hydrocarbons. Although this technique is considered to be a challenge; due to the complexity of understanding the situation in the subsurface, many modeling systems were developed and used.
Rifai and Rittaler (2005) presented a paper that showed methodologies for natural attenuation model development through data analysis and interpretation. They used BIOSCREEN as analytical model and BIOPLUME III as numerical natural attenuation and applied it on BTEX plume model to achieve their purpose. A petroleum product storage site located in central Texas was selected as study site, where decommission of three tanks took place, gasoline tank, diesel tank and waste oil tank. The investigation in the site assured the presence of dissolved hydrocarbon plume that migrated off site area. BIOSCREEN model requires input parameters such as seepage velocity, biodegradation parameters and source variables. However, the collected data about site geochemistry was not enough to estimate the electron acceptor capacity; therefore, first order decay was estimated for biodegradation of benzene. In contrast to BIOSCREEN, BIOPLUME III was able to simulate the excavation and its affect on the groundwater plume. They concluded that there are difficulties related to estimation of both, biodegradation rate in the field and source parameters essential for natural attenuation models.

Schäfer and Therrien (1995) used a three dimensional model to simulate the transport of reactive species and the biochemical interactions in former refinery site where xylene contamination was observed in groundwater. The distribution of the measured reactive species assured that xylene biodegradation took place in the site. Field observations suggested that aerobic and denitrifying bacteria were involved in xylene degradation. The results of the simulation showed low xylene concentration in side plume around specific well along with high microorganisms activity at the upstream boundary of the plume. In this well, mixing between contaminated water and oxygen and nitrate-rich water enhances the biodegradation rate. The biodegradation was enhanced by increasing electron acceptors flux at the wells. They concluded that the contribution of biodegradation in xylene removal is effective as extraction by well did. Also, they found the microbial
activity can be enhanced by injection of electron acceptors. However, there were many studies dealing with the effect of changing physical parameters on biodegradation include Keijzer et al. (1998), El-Kadi (2001) and El-Kadi (2007). Keijzer et al. (1998) suggested that changing physical and biochemical parameters will affect the behavior and efficiency of the injected electron acceptor through numerical simulation. Also, El-Kadi (2001) studied the effect of heat and the saturation on the biodegradation of hydrocarbon using SUTRA based model that can simulate multi species fate and transport combined with submodel for microbial growth in tidal aquifer. He concluded that the efficiency of biodegradation may reduce due to changes in water saturation using dissolved oxygen. However, he suggested that the cyclic wetting and drying in the case of subjecting the soil to aeration to supply oxygen can have positive impact on degradation. Also, he concluded that heat as inhabitation factor affected the biodegradation, the biomass concentration increased at the earlier time but with low rate.

Keijzer et al. (1998) used one dimensional model that simulates advective, dispersive transport, biotransformation and microbial growth and supplying electron acceptor is limiting factor for biodegradation. They distinguished three regimes, low oxygen consumption regime, intermediate and fast oxygen consumption regimes. They assumed that initial concentration of oxygen was zero \((t=0)\) and gasoline concentration was constant, while microbial mass was constant but small. First regime was characterized by low biodegradation rate because microbial mass was close to its initial value and could not consume the supplied oxygen. During the second regime, high oxygen concentration was consumed and rapid microbial growth was detected until balance between the supplied oxygen and the consumed oxygen. After balance occurred, no evaluation was needed for biodegradation kinetic, but instantaneous reaction between oxygen and gasoline is applicable. They found that interaction between advective mixing enhanced by
biodegradation and sorption of contaminant could affect the distribution of electron acceptor and contaminant. El-Kadi (2007) studied the effect of the variation in permeability in hydrocarbon biodegradation through stochastic analysis. He found that uncertainties in the results increased with the time which makes the decision of cleanup difficult.

Many studies indicated that the biodegradation of BETX depends on the terminal electron acceptor process (TEAP); the benzene degrades under aerobic condition with a rate higher than that of anaerobic conditions. Generally, BETX compounds could be biodegraded under aerobic condition but this is highly site specific. Although the degradation byproduct could be used as indicator for the biodegradation process, it does not quantify the loss in BETX mass due to biodegradation and therefore its comparison with the decrease in BETX concentration as the transport processes such as dispersion and adsorption are impossible (Schreiber et al., 2004).

Studies dealing with modeling hydrocarbons plume migration include Schirmer et al. (2000) and Schreiber et al. (2004). A study was done by Schreiber et al. (2004) at Fort McCoy field site, in Monroe, Wisconsin. The objective of this study was to use a 3D, multispecies reactive transport model, BioRedox-MT3DMS, in order to simulate the BETX plume at the site which has an average age of 20 years. This plume resulted from a leakage in an underground storage tank. Sensitivity analyses were performed to identify the losses in BETX mass due to increasing and decreasing despersivity, initial concentration of Fe III, effective porosity and plume age.

The idea of TEAP is that the electron acceptor which provides high energy will be consumed first before the lower in sequential manner. Therefore, methanoenic process will happen at the source. Simulation results showed that BETX losses at the field were due to the biodegradation under aerobic condition mainly, beside the biodegradation under the
reducing condition; Fe III and sulfate, and methanogenic condition. When the concentration of Fe III decreases, methanogenic conditions prevail. It is observed that the configuration of the plume depends on the effective porosity and the rate constants of the Fe III and methanogenic. However, the BETX losses depend on the plume age and rate constant under Fe III reducing condition (Schreiber et al., 2004).

Schreiber et al. (2004) studied the Fe-methane overlap. The results showed that the overlap depends on the effective porosity, initial concentration of Fe III, rate constants under Fe III and methanogenic conditions and the plume age.

Schirmer et al. (2000) carried out research on modeling the biodegradation of dissolved gasoline plume using laboratory experiment and field parameters. Laboratory and field scales were linked by using BIO3D model to simulate the dissolved gasoline plume at Canadian Force Base Borden. They used Monod parameters derived in the laboratory in the numerical model and compared the results with field measurements.

They found that degradation rates obtained using zero and first order decay models at laboratory scale were higher than that interpreted in the field because the laboratory conditions are usually optimized. Also the zero and the first order models can not describe the developed plume process because some of field parameters are ignored such as equilibrium at the field scale and non equilibrium sorption, availability of the nutrient and the spatial heterogeneities.

In most reactive transport models, vertical distribution of the contaminants concentration is ignored when applied in 2D simulations. However, the transversal vertical mixing caused by the seasonal hydrologic fluctuations could affect the length of the contaminant plume (Prommer et al., 2002).

Prommer et al. (2002) carried out a study using 3D advective transport numerical scheme called HMOC “hybrid method of characteristic” in which finite difference (FD)
and total variation diminishing (TVD) with a reactive transport model (MT3DMS) were used to simulate transient flow condition at a field site in Perth, Western Australia. They observed that HOMC scheme did not exhibit numerical dispersion under different transversal dispersivities. Results of TVD scheme were quite acceptable, while results of FD showed significant numerical dispersion. Further studies were performed to investigate the effect of increasing transient flow on the transverse dispersion and therefore on the natural attenuation rate. A simulation of concentration for advective, dispersive non reactive transport model was conducted and compared with linear equilibrium sorption model. It is observed that the later reduced the vertical plume movement and caused a reduction in the vertical spreading of the plume.

Prommer et al. (2002) studied the affect of the transient flow on reactive processes in the field using the reactive multicomponent transport model PHT3D. The model is based on the effect of the seasonal flow changes in increasing the transverse dispersion and mixing the substrate (toluene) and the electron acceptor (sulfate). As a result, biodegradation rate increases especially when sorption rates of the electron donor and electron acceptor are different. It is concluded that the coupled process of toluene sorption and seasonal changes played effective role in enhancing biodegradation of the contaminant.

2.3 Available Models for Contaminant Fate, Transport and Biodegradation in the Subsurface

The biodegradation process plays an effective role in decreasing the contaminant concentration in the subsurface. It is very difficult to quantify such process, however, using a modeling approach would help to follow the progress of the biodegradation process.

There are three main kinetic expressions for modeling biodegradation, Monod kinetics, first order decay kinetics and the instantaneous reaction kinetics (Bedient et al.,
Different expressions for Monod equations are found, including, single, double and the multiple. If the rate of the biodegradation is affected by the concentration of all substances involved in the reaction, then multiple Monod equation is used. If the substrate and one electron acceptor are considered, then double Monod equation is used. Single Monod equation with first order reaction is used when the concentration of substrate is smaller than the half saturation constant, $K_s$. However, zero order reaction is considered when $K_s$ is smaller than substrate concentration. Therefore, any incorrect values in the substrate concentration and half saturation constant will result in error in the model results. Although Monod kinetic helps in simulating and estimating the kinetic parameters of the biodegradation of BETX, it is observed that few of these parameters under anaerobic condition could be estimated by experiments (Schreiber et al., 2004).

Another widely used kinetic expression for modeling biodegradation is the first order decay:

$$C = C_0 e^{-kt}$$

where $C$ is the biodegraded contaminant concentration ($ML^{-3}$), $C_0$ is the initial concentration of the contaminant, $k$ is the rate constant and $t$ is the time. The first order decay is used mostly in modeling the biodegradation of dissolved hydrocarbons plumes. It is assumed that there is a direct proportional relationship between the concentration of the contaminant and the biodegradation rate. The first order decay coefficient is used as a parameter for calibration; the decay coefficient is changed until results of model match field data.

The third kinetic expression is the instantaneous reaction kinetic, "also called electron acceptor limited model". This model was suggested first by Borden and Bedient (1986), when modeling hydrocarbons degradation under aerobic condition. It was assumed that the rate of the contaminant biodegradation is very high, shorter time is needed for
oxygen consumption and microorganisms grow faster. This limited the use of such models. The biodegradation could be calculated using the relation;

\[ \Delta C_g = \frac{O}{F} \]  

(2.2)
where \( \Delta C_g \) is the change in the concentration of the contaminant as a result of the biodegradation, \( O \) is the oxygen concentration and \( F \) is the ratio of oxygen to the utilized contaminant (Bedient et al., 1990).

Biodegradation rates determined in the laboratory are not good representation of the real field situation because microbial processes are not explained well in the laboratory and the geochemistry of the site is different from one location to another. Determining the biodegradation rate in the field is coupled with understanding the complex transport processes. Reduction in contaminant concentration does not reflect biodegradation (Bedient et al., 1990).

Many of the researchers estimated the biodegradation rate using first order model. In 1996, Wiedemeir et al. estimated the decay rate from the normalized field data and then determined the decay constants after correction of BETX concentrations for the dispersion, dilution due to the recharge, volatization process and sorption depending on the tracer experiment (Bedient et al., 1990).

Another method to determine BETX decay rate is by assuming a steady state condition. In 1995, Buscheck and Alcantar developed a method considering one dimensional contaminant transport; advection, dispersion, sorption and biodegradation processes under steady state conditions while the volatization was not considered, and then made a regression of the contaminant concentration for the analytical solution. The following expression was obtained:

\[ \lambda = \left( \frac{V_c}{4 \alpha_x} \right) \left[ 1 + 2 \alpha_x \left( \frac{K}{V_x} \right)^2 \right]^{-1} \]  

(2.3)
where $\lambda$ is the $1^{\text{st}}$ order biological decay rate, $v_c$ is the retarded contaminant velocity in the x-direction, $\alpha_x$ is the dispersivity and $K/v_x$ is the slope of the line by plotting the contaminant concentration versus the distance downgradient (Bedient et al., 1990).

Rifai et al. (1988) and Chiang et al. (1989) determined the biodegradation constants at two field sites in Michigan by calculating the contaminant mass change with respect to the time depending on the average plume concentration

$$DM_t = C_{\text{avg},t} b n L W$$

where $DM_t$ is the dissolved mass at time $t$, $C_{\text{avg},t}$ is the average plume concentration, $b$ is the thickness of the aquifer, $n$ is the porosity, $L$ is the plume length and $W$ is the plume width (Bedient et al., 1990).

In 1997, Remediation Technologies Development Forum (RTDF) presented a graphic method for the site of concern based on preparing isoconcentration maps. The RTDF method draw perpendicular lines to the flow from different distance with respect to the source. After that, depending on the aquifer thickness and the velocity of the groundwater, the groundwater mass that passes each line annually is estimated (Bedient et al., 1990).

In order to understand the biodegradation process, many models were developed such as BIOPLUME which considers aerobic condition in 1D problems, BIO1D which considers aerobic and anaerobic conditions and BIOPLUM II which considers two dimensions, instantaneous and aerobic conditions.

There were many studies dealing with simulation of biodegradation such as McCarty et al. (1984), Sirivasan and Mercer (1988) and Schirmer et al. (2000). McCarty et al. (1984) developed Biofilm model assuming that the attached bacteria to the solid surface are fixed in one place and supplied by nutrients from the flowing groundwater. In the biofilm that is formed by those bacteria, two processes happen at the same time; substrate
utilization by the bacteria following Monod kinetic and the diffusion process of the substrate through the biofilm following Fick's Law. However, Sirivasan and Mercer (1988) developed a one-dimensional finite difference model, (BIO1D), to represent a biodegradation and sorption processes in saturated porous medium. It was extended from Borden and Bedient model (1986). The model was powerful because different boundary conditions and processes could be simulated. For example, aerobic biodegradation could be simulated using Monod kinetic. By using Michaelis-Menten, kinetics anaerobic biodegradation could be simulated. Also, Baek et al. (1989) developed BIOSOIL model to simulate the reduction of the contaminant concentration due to microbial activity in the unsaturated soil. It was observed that the unsaturated depth had less influence in the bioremediation. MacQuarrie et al. (1990) and MacQuarrie and Sudicky (1990) followed the same approach of Borden et al. (1986) and Rifai et al. (1988) to develop their model. They considered advection and dispersion processes and used dual Monod kinetic to describe biodegradation.

Schirmer et al. (2000) used BIO3D model to simulate the biodegradation of the dissolved gasoline at Canadian Force Base field experiment. The model originated from 2D principle direction model by MacQuarrie et al., (1990) and 3D single substrate finite element model under aerobic condition by Frind et al. (1989). The aerobic biodegradation process is governed by dual- Monod kinetic and the oxygen concentration is considered as a limiting factor. Groundwater flow and multiple mass transport equations are solved by Galerkin finite element technique and Leismann time- weighting method to keep matrix symmetry condition. It is observed that the availability of the oxygen as electron acceptor and the measured Monod parameters in the laboratory are important factors that affect the prediction of biodegradation rates of the BETX at the field scale. Schirmer et al. (2000) improved the work by adding the Haldane inhabitation term \( (S^2/ k_{ip}) \) in the substrate
equation to reduce the microbial growth rate as the degradation process depends on the availability of one electron acceptor (oxygen). They also considered the Haldane inhabitation term in the microbial population equation to control the growth of the microbes due to the existence of the substrate. They added the term \( (1 - M/M_{\text{max}}) \) to restrict the microbial growth, due to other reasons rather than the substrate utilization. They assumed linear sorption for the organic substrates.

On the other hand, Prommer et al. (2000) believed that the availability of the electron acceptors can control the biodegradation process of the organic contaminant; therefore the addition of the electron acceptors would enhance the biodegradation process. Kinzelbach et al. (1991) suggested that nitrate is the best electron acceptor when compared to oxygen and sulfate because oxygen is not available in sufficient amount and has low solubility, while sulfate is highly soluble in water but produces hydrogen sulfide.

Prommer et al. (2000) used a two dimensional model (PHTRN) to simulate the degradation of BETX compounds that result from NAPL contamination sources. This NAPL is assumed to be stationary and dissolved into the moving groundwater. They assumed that the uncontaminated groundwater contains oxygen, nitrate and sulfate and two types of bacteria namely; facultative aerobes/denitrifying and sulfate reducing bacteria. At the beginning, BETX undergoes aerobic degradation, when oxygen is depleted, degradation under nitrate condition will start and then microbes switch into sulfate reducing agent.

The Method of Characteristic (MOC) model is a two dimensional transport model developed by US Geologic Survey. BIOPLUME II was developed by modifying MOC. The main concept to modify MOC and develop BIOBLUME II is using a dual particle moyer procedure to model the oxygen and the contaminant transport in the subsurface. BIOPLUME II could be used to simulate biodegradation using two expressions; first order
decay and instantaneous reaction. The transport equation is solved twice for each time step to determine the distribution of the oxygen and the substrate. However, in 1997, Rifai et al. upgraded BIOPLUME II model into BIOPLUME III model, which was also based on MOC. In BIOPLUME III model, the biodegradation is simulated under aerobic and anaerobic conditions using different electron acceptors; oxygen, nitrate, Fe (III), sulfate and carbon dioxide. This model was basically developed to account for natural attenuation of organic contaminant in the subsurface. The biodegradation kinetic expression was used under aerobic and anaerobic condition with first order decay, instantaneous reaction and Monod kinetics. Beside the natural attenuation, the BIOPLUME III can simulate the bioremediation of the hydrocarbons contaminant in the subsurface and air sparging for low rate of air flow (Bedient et al., 1990).

Sun et al. (1996) developed Reactive Transport model in three dimensions (RT3D). This model could simulate multispecies, reactive transport in the subsurface. The model can simulate multiple sorbed and aqueous phase species with any reaction or natural attenuation and could be used to evaluate bioremediation. It can simulate different types of contaminants; including, heavy metals, explosives, petroleum hydrocarbons and chlorinated solvents (Bedient et al., 1990). However, Schreiber et al. (2004) suggested that information on terminal electron acceptor processes (TEAPs) is required for modeling reactive transport of contaminants in the subsurface. They used BioRedox-MT3DMS; a 3D, multispecies reactive transport model to simulate the biodegradation of BETX compounds and the distribution of the electron acceptors. The theoretical distribution of the TEAPs would produce the methanogenic condition in the source, followed by sulfate reducing agent, then ferric Fe (III) and finally the nitrate (Schreiber et al., 2004).
The conservative equation for the oxidation-reduction reaction in BioRedox is done by balancing the transferring rate of electrons from the electron donor with the electron acceptors.

The following are some of the available software models that simulate contaminant transport and biodegradation in groundwater:

**BIOMOC**

BIOMOC is a two-dimensional model that can simulate the transport and biotransformation of multiple reacting solutes. The program is general and flexible, allowing for any combination of biodegradation processes. A number of expressions for biological transformation rates have been included as options in the code. These include single, multiple, and minimum Monod kinetics and competitive, noncompetitive, and Haldane inhibition. The kinetic parameters can be formulated to simulate zero-order or first-order approximations of biodegradation rates. The growth and decay of several microbial populations performing the transformations is also accounted. The microbial growth can be disabled, limited by biomass inhibition, or limited by the availability of a specified nutrient.

**RT3D**

RT3D is a software package for simulating three-dimensional, multispecies, reactive transport in groundwater. The code is based on the 1997 version of MT3D (DOD_1.5), but has several extended reaction capabilities. RT3D can accommodate multiple sorbed and aqueous phase species with any reaction framework that the user wishes to define. RT3D can simulate a multitude of scenarios. For example, natural attenuation processes can be evaluated or an active remediation can be simulated. Simulations could potentially be applied to scenarios involving contaminants such as heavy metals, explosives, petroleum hydrocarbons, and/or chlorinated solvents. RT3D is
highly flexible. The users can enter their own reaction kinetic expressions or choose from a suite of eight preprogrammed reaction packages. Preprogrammed packages include: (1) Two Species Instantaneous Reaction (Hydrocarbon and Oxygen); (2) Instantaneous Hydrocarbon Biodegradation Using Multiple Electron Acceptors (O₂, NO₃⁻, Fe²⁺, SO₄²⁻, CH₄); (3) Kinetically Limited Hydrocarbon Biodegradation Using Multiple Electron Acceptors (O₂, NO₃⁻, Fe²⁺, SO₄²⁻, CH₄); (4) Kinetically Limited Reaction with Bacterial Transport (Hydrocarbon, Oxygen, and Bacteria); (5) Non-Equilibrium Sorption/Desorption (can also be used for Non-Aqueous Phase Liquid Dissolution); (6) Reductive, Anaerobic Biodegradation of PCE/TCE/DCE/VC.

**MOC3D**

This model simulates three-dimensional solute transport in flowing ground water. The model computes changes in concentration of a single dissolved chemical constituent over time that are caused by advective transport, hydrodynamic dispersion (including both mechanical dispersion and diffusion), mixing (or dilution) from fluid sources, and mathematically simple chemical reactions (including linear sorption, which is represented by a retardation factor, and decay). The model can also simulate ground-water age transport and the effects of double porosity and zero-order growth/loss.

**MF2K-GWT**

Three-dimensional ground-water flow and solute-transport model integrated with MODFLOW-2000. This model is an enhanced version of MODFLOW-2000 that incorporates the additional capability to simulate solute-transport processes and compute changes in concentration of a dissolved chemical constituent due to advection, hydrodynamic dispersion, retardation, decay, matrix diffusion, and mixing with multiple fluid sources.
CHAPTER 3

BU HASA LIQUID RECOVERY PLANT
Chapter 3

Bu Hasa Liquid Recovery Plant

3.1 Site Description and History

Bu Hasa area is located about 150 km southwest of the capital city, Abu Dhabi (Figure 3.1). Bu Hasa Liquid Recovery Plant (LRP) was established in late 1970s, and started production in 1980. The plant treats 11.2 million metric standard cubic meters per day (MMSCMD) of raw gas and produces approximately 11,000 tonnes of natural gas liquids daily. The inlet gas consists of 1,000 part per million (ppm) hydrogen sulfide (H₂S) and 0.03 to 0.05 carbon dioxide (CO₂). It is considered to be slightly sour, but the plant does not complete the sweetening process for the gas (Forrest and Arnell, 2001). Gases free from H₂S and CO₂ are called sweet. These kinds of gases undergo sweetening process to convert undesirable mercaptans into disulfide. Desulfurization process is required to convert the sulfur gas into elemental sulfur due to its toxicity.

In 2000, Abu Dhabi Industries Ltd. (GASCO) conducted phase II of the groundwater assessment study at Bu Hasa LRP to assess the extent of the hydrocarbons release in the subsurface of Liwa aquifer at Bu Hasa LRP. GASCO contracted Matrix Solutions Inc. to complete this assessment. Free and dissolved hydrocarbons were observed in the subsurface. In 2005, URS Corporation was contracted to undertake groundwater remediation at the site (URS Corporation, 2006).

3.2 Natural Gas Processing

The natural raw gas is extracted from the underground gas field through the wellhead. It undergoes purification processes in the natural gas processing plants. The characteristics of the natural raw gas depend on the type, depth of producing well, underground deposit location and the geologic properties of the area.
Figure 3.1: Bu Hasa Liquid Recovery Plant location (Source: Forrest and Arnell, 2001).
The main composition of the raw natural gas is methane. However, it may consist of varying amounts of heavier gaseous hydrocarbons such as ethane, propane, normal butane, isobutene, pentane and other higher molecular weight hydrocarbons. Also, the raw gas may contain acid gases like carbon dioxide and hydrogen sulfide beside other gases such as nitrogen and helium. Raw natural gas may also include water vapor and liquid water, liquid hydrocarbons, small amount of mercury and chloride. The purified raw natural gas must meet the quality standards and specifications established by the major pipelines transmission and distribution companies (Energy Information Administration, 2006).

There are mainly three types of wells that produce raw natural gas; associated gas well, non-associated gas well and condensate well. Associated gas well is the common one where oil and gas can be found separately or the gas is dissolved in the crude oil in the same reservoir. However, in the presence or absence of little amount of oil; it is termed as non-associated gas well. The condensate well describes the situation of small hydrocarbon molecules presence in gaseous state at underground pressure which becomes liquid at normal atmospheric pressure (Energy Information Administration, 2006).

The processing of well gas into pipeline quality dry natural gas requires several steps to remove oil, water, elements such as sulfur, helium and carbon dioxide as well as the removal of natural gas liquids (NGLs). There are important stages prior to the removal processes of oil, water and elements; these stages take place near or at the wellhead. These stages require scrubbers and heaters installation. The scrubbers are used to remove sand and other large particle impurities. The heaters are used to assure that the temperature of the natural gas does not drop down and avoid the formation of the hydrate with the water vapor content of the gas stream and therefore, obstacles the movement of the natural gas through the pipes and valves (Energy Information Administration, 2006).
The type of techniques and the number of stages used in the process of pipeline quality natural gas depend on the source and the composition of the wellhead production stream. In some situations, different steps may be integrated into one unit, or performed in different order, or may not be required.

The first stage of the gas processing (Figure 3.2) is the gas-oil separators. Due to releasing pressure; natural separation of the gas from the oil using conventional closed tank takes place. The gaseous hydrocarbons are separated from the heavier hydrocarbons by gravity difference. However, in other cases a multistage of gas-oil separation is required to separate the gas stream from the crude oil. The second stage is the condensate separator. It deals with the removal of the condensate from the gas stream. This process usually takes place at the wellhead by using the mechanical separators. The extracted condensate is routed to on-site storage tanks.

Dehydration process is the next stage to assure no hydrates are formed by removing the water from the produced natural gas through several methods. Ethylene glycol (glycol injection) is used as an absorption system to remove the water and other solids from the gas stream.

There is another stage to remove the hydrogen sulfide, carbon dioxide, water vapor, helium and oxygen which is called contaminant removal. The common technique for this purpose is by passing the flow through tower containing an amine solution.

The following stage is the nitrogen extraction in which the stream is routed to Nitrogen Rejection Unit (NRU) through a column and a brazed aluminum plate fin heat exchanger. There is another type of NRU that separates methane and heavier hydrocarbons from nitrogen using an absorbent solvent.

The fractionation step is the last stage where the separation of the natural gas liquids remaining in the gas steam takes place depending on the difference of the boiling
Figure 3.2: Generalized natural gas processing schematic (Source: Energy Information Administration, 2006).
point of individual hydrocarbons in the gas stream. The gas stream is passed through several towers where the heating units increase the stream temperature and cause the separation that exist the tower into holding tank. (Energy Information Administration, 2006).

In the liquefying process, the natural gas is stored and transported through the pipelines for a long distance in a form of liquid. Turning the natural gas into liquid form is called refrigeration process in the liquefaction plant by which the volume is reduced by a factor of 610. Later on, the liquefied natural gas (LNG) is converted into gas state through a regasifier (Energy Market Authority, 2005).

Bu Haṣa LRP is receiving associated gas from Abu Dhabi Company for Onshore Oil Operations (ADCO) through pipelines in three streams; high pressure, intermediate pressure and low pressure. The plant removes the natural gas liquids from the incoming gas through different processes. The incoming streams are boosted to the initial processing pressures by using compressors. The refrigeration, pressure differentials and fractionation processes are used for the condensation and the separation of the natural gas liquid. After compression, the two parallel gas processing trains which have a total capacity of 15.3 million metric standard cubic meter per day (MMSCMD) refrigerate the gas to a temperature as low as -87 °C to ensure a high propane recovery which is above 99%.

Later on, the natural gas liquids are collected and transported through the pipeline to Abu Dhabi Gas Industries (GAṢCO) facilities in Ruwais for additional processes and shipping. The dehydration process takes place onsite to remove the water from the gas and liquid streams. The removed water is treated and/or disposed of on site. The residual lean gas is sent to by pipes to Abu Dhabi National Oil Company (ADNOC) and ADCO facilities for use as fuel gas or for reinjection operation in the petroleum reservoirs (Forrest and Arnell, 2001).
There are many facilities in Bu Hasa LRP (Figure 3.3); process buildings, compressors, chillers, aboveground and underground storage tanks, pipelines, burn/disposal pits and water treatment facilities. Also there is a camp near to the plant for accommodating 530 persons. The camp includes a sewage treatment facility. There are eight source wells (RW1 to RW8) located 40 m below the land surface of liwa aquifer.

The water well is used for camp requirements rather than drinking such as irrigation and washing. Water wastes containing hydrocarbons resulted from the plant processing are disposed at the site and the area overlying liwa aquifer (Forrest and Arnell, 2001).

There are three unlined sizable burn pits located east of the plant. The most western one is called former warm blowdown area that receives knock out liquids, while the other two pits receive mainly flare gases with some light hydrocarbons such as C₃ and C₄ components. The visual observations of the former warm blowdown area indicate the existence of the hydrocarbon within the fenced perimeter. The collected soil samples from this area had hydrocarbon odor and they were stained black, dark brown and light brown. They can be distinguished from the non-effected soils having yellow, reddish-yellow and yellowish-brown color (Forrest and Arnell, 2001).

Changes in the temperature and pressure in the gas gathering and gas compression sections resulted in liquid wastes; water and hydrocarbons which are knocked out in the vessels. The hydrocarbon is recovered as natural gas liquids while the residual water is disposed of on site. Also there is knock out drums upstream that receives any liquid from the flare systems to ensure moving dry gases to the flare (GASCO, 2006).
Figure 3.3: Bu Hasa Liquid Recovery plant (Source: www.gasco.ae, 2008).
The knock out of the processed water from the gas gathering and gas compression sections is sent to a sewage treatment plant. At this point, there were two problems related to the quality of the disposed water; the separation of the hydrocarbon and its disposal at the sewage treatment plant after the separation. Therefore, there is a vessel identified as Process Water Drum to ensure proper separation of the oil and water as well as to degasify the water/hydrocarbon before the disposal to sewage treatment plant (GASCO, 2006).

3.3 Phases of Hydrocarbons in Bu Hasa Field

Matrix (2001) indicated the presence of free phase hydrocarbons floating on the water table in monitoring wells 98-2, 00-2, 00-3 and 00-5. The thickness of free hydrocarbons in well 98-2 was 1.21 m. In well 00-2, it was 1.65 m, and in well 00-3 it was 1 m (Figure 3.4).

The presence of free phase hydrocarbons stain on the top of the water table is considered as a continuous source of groundwater contamination. The partial dissolution of the dissolved constituents results in the formation of the dissolved hydrocarbon plumes. Forest and Arnerll (2001) reported that a volume of 2,830 m$^3$ of free phase hydrocarbon was detected in the former warm blowdown area. URS Corporation (2005) estimated the volume of free phase hydrocarbon as 10,225 m$^3$. Forest and Arnerll reported also the presence of 0.03 mg/l of the dissolved benzene in monitoring well 00-8 (Figure 3.4).
Figure 3.4: The dissolved hydrocarbon distribution in former blowdown area (Source: Forrest and Arnell, 2001).
Figure 3.4: The dissolved hydrocarbon distribution in former blowdown area (Source: Forrest and Arnell, 2001).
CHAPTER 4

MODELING CONTAMINANT TRANSPORT IN LIWA AQUIFER
Chapter 4

Modeling Contaminant Transport in Liwa Aquifer

4.1 Introduction

BTEX compounds; benzene, toluene, ethylbenzene and xylene are partially soluble monoaromatic hydrocarbons. They are relatively mobile in groundwater and have high water-air partition coefficient. When the contaminated water, containing hydrocarbons, in Bu Hasa LRP is released on the surface, it moves vertically toward the saturated zone under the force of gravity. The conceptual model for the dissolved hydrocarbons transport includes the dissolution, migration, retardation and biodegradation.

4.2 METABIOTRANS

4.2.1 Model Descriptions

The model used in this study is called METABIOTRANS (Mohammed, 2001). METABIOTRANS is a 3-D finite element model. It simulates the transport of multiple solutes in anisotropic, heterogeneous saturated aquifers, as influenced by advection, dispersion, adsorption, and biodegradation/biotransformation (Mohamed and Hatfield, 2005, Mohamed et al., 2006, Mohamed et al., 2007). Biotransformation follows the Monod kinetics equation modified to include the effect of electron acceptor availability. Solutes dissolved in the aqueous phase may adsorb to the solid phase following a linear isotherm, or they may diffuse into microbial phase where biotransformation occurs.

METABIOTRANS has the following features:

1- Multi-component aqueous advective and dispersive transport in saturated groundwater aquifers.

2- Simulates 1-D, 2-D, and 3-D problems.

3- Linear adsorption isotherm for all the solutes (electron donors and acceptors)

4- Biodegradation/biotransformation using Monod kinetics.
5- Spatial variation in recharge/injection.

6- Multiple pumping and/or injecting wells.

7- Simulation of heterogeneous and/or anisotropic porous media.

8- Biotransformation by multi-bacterial-species.

9- Two inhibition factors that affect the behavior of the bacterial species.

In METABIOTRANS, any number of solutes can be simulated. In addition, the microbial phase is assumed to consist of any number of independent bacterial species, which have the ability to reduce electron acceptors and oxidize electron donors. These bacterial species are assumed to exist as scattered microcolonies attached to the porous media. METABIOTRANS assumes that mobile organisms have a negligible effect compared to the attached ones. Microbial growth is assumed to depend on the availability of substrates (electron donors), nutrients, and the electron acceptor being reduced.

4.2.2 METABIOTRANS Governing Equations

Transport Equations

Aqueous phase transport is described by the advection-dispersion equation; the first for electron donors and the second for electron acceptors. These equations are coupled through source/sink terms for biodegradation. For each electron donor or electron acceptor the transport equation may be written as (Borden and Bedient, 1986):

\[ R_s \frac{\partial S_k}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial S}{\partial x_j} \right) - v_i \frac{\partial S_k}{\partial x_i} + Q_{bio} \]  

(4.1)

\[ R_s \frac{\partial A_k}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial A}{\partial x_j} \right) - v_i \frac{\partial A_k}{\partial x_i} + Q_{bio} \]  

(4.2)

where \( S \) is the aqueous phase concentration (ML\(^{-3}\)) for electron donor (contaminant), \( A \) is the aqueous phase concentration (ML\(^{-3}\)) for the electron acceptor, \( v_i \) is the average pore water velocity in the \( i \) direction (LT\(^{-1}\)), \( x_i \) is the distance in the \( i \) direction (i = 1, 2 or \( x_i = x \), 3).
y) (I.) $D_{ij}$ is the 2nd order tensor for hydrodynamic dispersion ($L^2T^{-1}$), $Q^{bo}$ is a biodegradation sink term ($ML^{-3}T^{-1}$), $R$ is the retardation factor (dimensionless), and $t$ is time ($T$).

**Source/sink Equations**

The biodegradation source/sink terms are evaluated by (Borden and Bedient, 1986)

\[
\frac{dS}{dt} = Q^{bo}_{s} (S, A, M) = -\frac{M \chi_s}{\theta} 
\]

\[
\frac{dA}{dt} = Q^{bo}_{a} (S, A, M) = -\frac{M \chi_a}{\theta} 
\]

where $M$ is the microbial biomass concentration ($ML^{-3}$), $\theta$ is the aquifer porosity (dimensionless), and $\chi_s$ and $\chi_a$ are the utilization rate of electron donor and electron acceptor, respectively, by the bacterial species ($T^{-1}$).

**Utilization Equations**

Utilization rates are related to the specific growth rates ($\mu$) for the bacterial species utilizing electron donor and electron acceptor ($T^{-1}$). Utilization of electron donor and electron acceptor by the bacterial species can be written as follows (Borden and Bedient, 1986):

\[
\chi_s = \frac{\mu}{Y_s} 
\]

\[
\chi_a = \frac{\mu}{Y_a} 
\]

where $Y_s$ and $Y_a$ are the yield coefficient (dimensionless) representing the mass of bacterial species produced per unit mass utilized of electron donor and electron acceptor, respectively.

**Microbial Growth Equations**

The specific growth rate of the microbial species utilizing electron donor and
electron acceptor can be written as (Borden and Bedient, 1986):

$$\mu = \mu_{\text{max}} \left( \frac{A}{(K_a + A)} \right) \left( \frac{S}{(K_s + S)} \right)$$  \hspace{1cm} (4.7)

where $\mu_{\text{max}}$ is the microbial maximum specific growth rate ($\text{T}^{-1}$), $K_s$ and $K_a$ are the half saturation coefficient for electron donor and electron acceptor, respectively, (ML$^{-3}$). The mass balance equation for growth and death of the microbial population can be written as:

$$\frac{dM}{dt} = M(\mu - B)$$  \hspace{1cm} (4.8)

where $B$ is the first order decay rate which accounts for cell death.

4.2.3 Input and Output

In preparation for using METABIOTRANS, the user should prepare a data file containing the following:

1. Problem dimensions: 1, 2 or 3-D.

2. Discretization:
   - Nodes data: node number and its corresponding Cartesian coordination.
   - Elements data: number of each element and the corresponding nodal numbers.
   - Materials data: the different aquifer material properties at each element.

3. Boundary conditions:
   - Flow boundary conditions:
     a. Specified head.
     b. Specified flow.
   - Transport boundary conditions:
     c. Specified solute concentration.
     d. Specified solute flux.

4. Initial conditions for transport equation.

5. Injection/discharge data:
a. Number of injection/discharge wells.

b. Time functions

6. Solutes data:
   a. Number of solutes.
   b. Chemical properties for each solute.

7. Bacterial species data:
   a. Number of bacterial species.
   b. Solutes that are being utilized by each bacterial species.
   c. Growth parameters for each bacterial species.

METABIOSIS uses time splitting algorithm to solve the system of non-linear partial differential equations. First, the model solves the steady-state saturated groundwater equations for the head values at each node in the problem domain. Secondly, the flow velocity is calculated in each element. Then, for each time step, the transport equations are solved (without the biological terms), for each solute, using the velocity values obtained previously. For each bacterial species, solutes and bacterial concentration values are then modified by solving the biological equations using the fourth-order Runge Kutta method with smaller time steps (1% of the original time step). After modifying all the solutes and bacterial concentration values, the model moves to the next time step. The model terminates when the specified number of time steps is completed. Several output files are then created, which include the nodal elemental values of:

1. Initial and boundary condition values of hydraulic head and solute concentration.

2. Hydraulic head.

3. Flow velocity.

4. Solute concentration for each solute at the specified time steps.

5. Microbial concentrations for each microbial species at the specified time steps.

61
6. Total mass of the solutes and bacterial species at each time step.

4.3 Geology of Bu Hasa Field

The United States Geological Survey conducted a study on the hydrogeologic unit of Bu Hasa field. There are two separated main hydrogeologic units named the groundwater reservoir and the petroleum reservoir (Figure 4.1). The groundwater reservoir is composed of a number of aquifers that extend to a depth of about 1,640 m below the ground surface. The unconfined Liwa aquifer is the shallowest one and is used as the main source of camp water supply. The water table of Liwa aquifer is at a depth of 40 m, and the productivity of the upper portion of the aquifer is high. The transmissivity varies between 2.4 and $7.5 \times 10^3$ and the total dissolved solids (TDS) vary between 3,000 and 17,000 mg/l. The underlying aquifers have higher salinity (70,000-100,000 mg/l) as compared to the Liwa aquifer (Forrest and Arnell, 2001). The vertical flow of water is prevented due to the presence of evaporite-rich Loer Fars confining layer which has a TDS value of 30,000 mg/l (Forrest and Arnell, 2001).

4.4 Precipitation and Recharge

The mean rainfall in the UAE is about 100mm/year, covering approximately an area of 77,700 km² (Forrest and Arnell, 2001). The rainfall occurs during winter time; mostly between December and March. February is considered the wettest month on average, however, the rainfall distribution vary over time. The mean annual rainfall in the Western region is less than that in the Eastern region by about 30 mm/year (Al Katheeri, 2007). The runoff represents about 1.9% of the mean annual rainfall, while the recharge represents about 1.5%. About 96.6% of the rainfall is lost due to the evaporation. It was indicated from the water elevation data that the direction of the regional groundwater flow in Liwa aquifer is to the northwest of Bu Hasa LRP area (Forrest and Arnell, 2001).
Figure 4.1: The lithology and hydrostratigraphy of Liwa aquifer (Source: Forrest and Arnell, 2001).
4.5 Groundwater

The groundwater reservoirs in Western region are dune and sand dunes aquifers. They cover a 2,400 km$^2$ in the Greater Liwa area. Fresh groundwater can be found in the shallowest aquifers and the salinity increases with the depth (Al Katheeri, 2007).

The continuous pumping of water from Bu Hasa LRP supply wells resulted in a significant depression in the water table of Liwa aquifer. From 1978 to 1998, an apparent drop in the water table elevation by about 1 m could be observed. The depression in the water table surface could be clearly noticed in the area near source wells (RW1 to RW6) as shown in (Figure 4.2).

4.6 Model Setup

4.6.1 Model Domain

The model domain is shown in (Figure 4.3). In this area, an estimated volume (10,225 m$^3$) of free phase hydrocarbons has been detected (URS Corporation, 2005). The model domain covers an area of approximately 292250 m$^2$, it extends 350 m in x-direction and 835 m in y-direction (Figure 4.3). A two dimensional finite element grid of 11690 elements is used for spatial discretization of the study area. The finite element mesh is constructed of quadrilateral elements; each element cell has 5 m length and 5 m width. The number of the elements in the x-direction is 70 and in y-direction is 167 elements (Figure 4.5). The domain was selected to contain the source area in the southeast corner and the nearest production well (RW1) in northwest corner. Section A-Á in Figure 4.4 represents conceptual cross sectional view of hydrocarbon occurrence (Forest and Arnell, 2001).

4.6.2 Groundwater Flow Model

The hydraulic head gradient of the groundwater in Bu Hasa field is variable. The head gradient increases toward the pumping well; therefore the groundwater velocity also
Figure 4.2: Groundwater elevation in Bu Hasa Field (Source: Forrest and Arnell, 2001).

Figure 4.3: The site plan of Bu Hasa Liquid Recovery Plant showing study domain (Source: Forrest and Arnell, 2001).
Figure 4.4: Conceptual cross sectional view of hydrocarbon occurrence (Source: Forest and Arnell, 2001).
Figure 4.5: Discretization of the study domain
increases in the same area. The hydraulic head gradient between the former warm blowdown area and the supply water well RW1 is almost 0.25%. The effective porosity is 0.3 and the hydraulic conductivity is $1 \times 10^{-4}$ m/s. The average linear velocity is estimated to be 25 m/year (Forest and Arnell, 2001). The water level elevation in monitoring wells indicated that the direction of the groundwater flow in Liwa aquifer is to the northwest in the area of Bu Hasa LRP site (Figure 4.6) (Forest and Arnell, 2001). Due to lack of available data regarding pumping rates and flow boundary conditions; the flow module in METABIOTRANS was not used to calculate the groundwater velocity. Instead, the estimated magnitude and direction of groundwater flow by Forest and Arnell are used in the transport module of METABIOTRANS to simulate the transport of the dissolved benzene.

4.6.3 Transport Model

The contaminated plume is expected to migrate from the source zone in the direction of groundwater as estimated by Forest and Arnell (2001). The exact direction of groundwater was estimated using the hydraulic head map (Figure 4.6). Due to lack of data collected from the site, the physical, chemical and biological input parameters along with the initial and boundary conditions were selected to best qualitatively match the field condition. Details are given in the following section

Assuming ideal NAPL mixture in contact with water, the aqueous phase concentration of a component in NAPL is equal to the product of its pure aqueous solubility and its mole fraction. McNab and others (1997) assumed that the mole fraction of benzene is equal to 0.5% of its weight fraction, the pure benzene solubility is equal to 1770 mg/l; therefore the aqueous phase concentration of the benzene in NAPL mixture is 8.85 mg/l. However, Johnson et al. (2000) reported that the equilibrium concentration of BETX resulted from typical gasoline mixture in contact with water has benzene
Figure 4.6: Groundwater flow direction in the study domain of Liwa aquifer (Source: Forrest and Arnell, 2001).
concentration of 18 mg/l. Assuming the benzene concentration is equal to 8.5 mg/l and the mean annual rainfall within the UAE is approximately 100 mm/year, the mass flux of benzene will be equal to 2.3 mg/day. This value will be used as a constant flux over the whole source zone because this value is highly dependent on the rainfall which is not constant over the years. Sensitivity analysis study was performed in chapter five to demonstrate the effect of mass flux variation on the migration of contaminant plume.

The shortage of data in the study area led to the use of common hydrogeological parameters of sandy aquifers. The groundwater flow is mostly in the y-direction (northwest). The longitudinal dispersivity is selected to be 2.5 m and the transverse dispersivity is taken as 0.25 m (Weaver and Charbeneau (2000) suggested $\alpha_T$ equals 0.23 m). Also the effective porosity is assumed to be 0.3 and the bulk density is suggested as 1.67 g/cm$^3$. The retardation factor is set equal to 2 and the calculated distribution coefficient is set equal to 0.18 (e.g. Clement et al., 2004; Choi et al., 2005).

The biological parameters used in this chapter are set as given in table 4.1. These parameters are selected based on literature values for these parameters which vary depending on the contaminant and bacteria species (Table 4.2).

Table 4.1: Input data for biological parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum bacterial specific growth rate ($\mu_{\text{max}}$)</td>
<td>0.005 day$^{-1}$</td>
</tr>
<tr>
<td>Microbial decay coefficient (B)</td>
<td>0</td>
</tr>
<tr>
<td>Biomass initial concentration (Mo)</td>
<td>0.001 mg/l</td>
</tr>
<tr>
<td>Yield coefficient (Ys)</td>
<td>0.01</td>
</tr>
<tr>
<td>Half saturation coefficient ($K_s$)</td>
<td>250 mg/l</td>
</tr>
</tbody>
</table>
Table 4.2: Literature values for biological parameters

<table>
<thead>
<tr>
<th>Reference</th>
<th>Parameter</th>
<th>Value/range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schaf er (2001)</td>
<td>$\mu_{\text{max}}$, $K_s$, $Y_s$, $B$</td>
<td>$0.004167 \text{ h}^{-1}$, $0.2-70 \text{ mg/l}$, $0.02-0.1$</td>
</tr>
<tr>
<td>Brusseau et al. (1999)</td>
<td>$\mu_{\text{max}}$, $K_s$, $Y_s$, $B$</td>
<td>$0.004167 \text{ h}^{-1}$, $1-3 \text{ mg/l}$, $0.8$ Neglected in most simulation, they concluded that effect of $B$ becomes measurable when $B &gt; 0.1\mu_{\text{max}}$</td>
</tr>
<tr>
<td>Schaf er et al. (1998)</td>
<td>$\mu_{\text{max}}$, $K_s$, $Y_s$, $B$</td>
<td>$0.04-0.2 \text{ h}^{-1}$, $0.003-1.25 \text{ mmol/l}$, $0.02-0.1$ Neglected</td>
</tr>
<tr>
<td>Kindred and Celia (1989)</td>
<td>$\mu_{\text{max}}$, $K$</td>
<td>$0.004-0.04 \text{ h}^{-1}$, $0.01-0.1 \text{ mg/l}$</td>
</tr>
<tr>
<td>Parlange et al. (1984) and Essaid and Bekins (1995)</td>
<td>$\mu_{\text{max}}$, $K_s$, $B$</td>
<td>$2E-5 \text{ h}^{-1}$, $0.5 \text{ mmol/l}$ Neglected</td>
</tr>
<tr>
<td>Salvage and Yeh (1998)</td>
<td>$\mu_{\text{max}}$, $K_s$, $K_s$, $Y_s$, $B$</td>
<td>$0.0387-1.35 \text{ h}^{-1}$, $1E_4-2.2E_3 \text{ mmol/l}$, $7.5 \text{ mg/l}$, $1.3E_4-2.0$ Neglected</td>
</tr>
<tr>
<td>Schirmer et al. (2000)</td>
<td>$\mu_{\text{max}}$, $K_s$, $B$</td>
<td>$0.0083-0.172 \text{ h}^{-1}$, $0.1-2.0 \text{ mg/l}$ Neglected</td>
</tr>
<tr>
<td>Wang and Shen (1997)</td>
<td>$\mu_{\text{max}}$, $K_s$, $Y_s$</td>
<td>$0.02745-0.064345 \text{ h}^{-1}$, $5.43-8.64 \text{ mg/l}$, $1.39E11-4.80E11 (\text{cell/mg})$</td>
</tr>
<tr>
<td>Schirmer et al. (1999)</td>
<td>$\mu_{\text{max}}$, $K_s$, $B$</td>
<td>$0.172-0.1875 \text{ h}^{-1}$, $0.79-4.7 \text{ mg/l}$ Neglected</td>
</tr>
</tbody>
</table>

4.7 Base Cases

Modeling two simulations are considered as base cases for later comparisons in chapter five and six. These two cases represent the expected scenario of the plume
migration. In the first one, the model is used to simulate the benzene plume in the absence of bacteria assuming no bioremediation. In the second base case, natural attenuation is simulated. In both cases, it is assumed that the benzene mass flux through the top boundary is equal to 2.3 mg/day as discussed earlier.

The comparison between the contaminant plume in both cases is shown in Figure 4.7. At earlier times (less than ten years), the effect of the bioremediation was slightly noticed near the source zone, but became obvious after twenty years. After thirty years, the source zone is exposed to high biodegradation rate, while some of the contaminant escaped. It is noticeable that the highest value of contaminant concentration is continuously decreasing due to bioremediation. Also, more biodegradation is observed at late times especially near the source zone.

Natural attenuation starts to be effective after twenty years. The high simulated biodegradation rate is probably due to the relatively low groundwater velocity. With low groundwater velocity, plume is exposed longer to bacterial species and; therefore, more contaminant mass is biodegraded near the source zone. Despite this, the groundwater velocity was not slow enough to stop some of the contaminant to escape away from the source zone. It is clear also that most of biodegradation occurs at the tailing edges of the plume (Figure 4.7). This is probably because the leading edge of the plume stimulates bacteria and by the time the tailing edge of the plume passes through the same location it encounters higher bacterial concentration.

Figure 4.8 shows the biomass concentration. After twenty years, the bacterial growth rate increased especially in the plume core, the maximum biomass concentration is noticeably increased compared to that generated at earlier time. Ten years later (at thirty years), the bacteria is stimulated and grow rapidly especially in the tailing edge of benzene plume, while some of the contaminant escaped (Figure 4.8). After forty years, more
Figure 4.7: Benzene plume base case in the absence and the presence of bacteria.
Figure 4.8: Biomass contours for the benzene plume base case.
biomass is observed in the plume core (Figure 4.7). Still some of the contaminant escaped to the leading edge of the plume. After fifty years, high biomass concentration accumulated near the tailing edge of the plume.

Figure 4.9 supports the previous finding that is biodegradation process is more effective after ten years. The rate of contaminant mass loss was very low before ten years due to slow biomass growth. Then, the microbial growth rate increased and was highest between ten and twenty years. That's why highest contaminant mass loss is observed in this period (Figure 4.9). By the end of twenty years, about 70% of the contaminant mass was biodegraded. Between twenty and fifty years, high biomass concentration is observed, but the high reduction in the contaminant mass (about 90% of contaminant mass) reduces the biodegradation rate again. In summary, highest contaminant biodegradation occurs near source zone between ten and twenty years which results in the highest contaminant mass loss.
CHAPTER 5
SENSITIVITY ANALYSIS STUDY OF NATURAL ATTENUATION
Chapter 5

Sensitivity Analysis Study of Natural Attenuation

A sensitivity analysis study was performed to investigate the sensitivity of contaminant plume migration to several physical and biological parameters in Bu Hasa Liquid Recovery Plant. The presence of electron acceptor was assumed. These parameters include the dispersivity coefficient ($\alpha$), the maximum specific growth rate ($\mu_{\text{max}}$), the initial biomass concentration ($M_0$), the microbial decay factor ($B$), the contaminant half saturation coefficient ($K_s$) and the microbial yield coefficient ($Y_s$). Also the effect of applying different values of flux in the presence and the absence of bacteria is examined.

Table 5.1 presents the different cases of sensitivity analysis simulations.

Table 5.1: Simulations of sensitivity analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base case</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersivities ($\alpha_L &amp; \alpha_T$)</td>
<td>2.5 &amp; 0.25 m</td>
<td>1.25 &amp; 0.125 m</td>
<td>-</td>
<td>5.0 &amp; 0.5 m</td>
<td>10.0 &amp; 0.1 m</td>
</tr>
<tr>
<td>Contaminant mass flux</td>
<td>2.3 mg/day</td>
<td>5 mg/day</td>
<td>15 mg/day</td>
<td>30 mg/day</td>
<td>60 mg/day</td>
</tr>
<tr>
<td>Bacterial maximum specific growth rate ($\mu_{\text{max}}$)</td>
<td>0.005 day$^{-1}$</td>
<td>0.0025 day$^{-1}$</td>
<td>0.00125 day$^{-1}$</td>
<td>0.01 day$^{-1}$</td>
<td>0.02 day$^{-1}$</td>
</tr>
<tr>
<td>Initial biomass concentration ($M_0$)</td>
<td>0.001 mg/l</td>
<td>0.0005 mg/l</td>
<td>0.00025 mg/l</td>
<td>0.002 mg/l</td>
<td>0.004 mg/l</td>
</tr>
<tr>
<td>Bacterial decay rate ($B$)</td>
<td>0</td>
<td>0.000125</td>
<td>0.0005</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Half saturation constant ($K_s$)</td>
<td>250 mg/l</td>
<td>125 mg/l</td>
<td>63 mg/l</td>
<td>500 mg/l</td>
<td>1000 mg/l</td>
</tr>
<tr>
<td>Microbial yield coefficient ($Y_s$)</td>
<td>0.01</td>
<td>0.005</td>
<td>0.0025</td>
<td>0.02</td>
<td>0.04</td>
</tr>
</tbody>
</table>
5.1 Sensitivity of Natural Attenuation to Changes in Dispersivity

METABIOTRANS is used to investigate the influence of increasing or decreasing the longitudinal and the transverse dispersivity coefficients of the aquifer on the contaminant concentration through three scenarios. The values 2.5 m and 0.25 m of $a_L$ and $a_T$ were assumed, respectively in the base case. The effects of increasing $a$ by 25% (case 3) and 50% (case 4) of its base value and decreasing it by 50% (case 1) on the contaminant concentration were examined and the results were compared with the base case result. Figure 5.1a shows the contaminant contour lines after ten, twenty and forty years for the first scenario when $a_L$ and $a_T$ have values of 1.25 m and 0.125 m, respectively. It is observed that since the earlier time, some changes occurred in the source zone core. These changes became obvious after twenty years (Figure 5.2a). Applying 50% less than $a$ of the base case value caused low contaminant dispersion; therefore the contaminant spread slowly in the plume zone as compared to the base case after forty years. In the second scenario, increasing $a$ in scenario one by 50% caused faster spreading of the contaminant contour in the plume zone since the earlier time.
Figure 5.1: Effect of decreasing (a) and increasing (b) dispersivity on the contaminant concentration.
Figure 5.1b shows the effects of increasing $\alpha$ to two and four folds of the base scenario values on the contaminant contour. When the values of $\alpha_L$ and $\alpha_T$ were 10 m and 1 m, respectively, the plume extended to the plume zone faster than the base case after ten years. However, using values of 5 and 0.5 for $\alpha_L$ and $\alpha_T$, respectively, caused the plume to extend for less distance than the highest value of dispersivity. Aquifer with higher values of dispersivities may have lower biodegradation rates as whole. This may cause the plume to reach the production well faster leaving less time for natural attenuation. Figure 5.1b shows that with highest values of dispersivities, the leading edge of the plume reached about 750 m along y-axis after forty years, whereas it reached 700 m in the base case.

Figure 5.2a shows the effect of decreasing the dispersivity on the biomass concentration. When $\alpha_L$ and $\alpha_T$ values equal to 1.25 and 0.125, respectively, less biomass accumulation in the plume core is modeled, but higher than the base case.

The effect of increasing the dispersivity to four times the base value appeared after ten year (Figure 5.2b). Less biomass concentration is observed in the plume core, while in the base case, the growth of bacteria was higher in the plume core (Figure 5.2b).

The effect of decreasing the dispersivity value by 50% after twenty years is shown in Figure 5.3a. In the case of using $\alpha_L$ and $\alpha_T$ values equal to 1.25 and 0.125, respectively, more biomass growth in the plume core is simulated as compared the base case (Figure 5.3a).

The effect of increasing the dispersivity four and two times the base value after twenty years is shown in Figure 5.3b. When $\alpha_L$ and $\alpha_T$ values equal to 10 and 1, respectively, more bacterial growth is observed in the bottom of the plume. This may be due to the effect of high dispersion coefficient as more contaminant spread out. Also, low biomass concentration in the plume core can be noticed as compared to the other two cases (Figure 5.3b).

80
Figure 5.2: Effect of decreasing (a) and increasing (b) dispersivity on the biomass concentration after 10 years.
Figure 5.3: (a) Effect of decreasing (a) and increasing (b) dispersivity on the biomass concentration after 20 years.
Figure 5.3: (a) Effect of decreasing (a) and increasing (b) dispersivity on the biomass concentration after 20 years.
After forty years, the bacterial growth in the core and the tailing fringe of the plume increased in the case when $\alpha_L$ and $\alpha_T$ values equal to 1.25 and 0.125, respectively (Figure 5.4a).

Figures 5.4b shows the results of using high dispersivity coefficient values. The bacterial growth in the bottom of plume become obvious after forty years when $\alpha_L$ and $\alpha_T$ values equal to 10 and 1, respectively. The biomass concentration increased in the plume core and the tailing edge when using $\alpha_L$ and $\alpha_T$ values as 5 and 0.5, respectively.

Figure 5.5 shows the effect of the dispersivity on the contaminant mass. In all simulations, biodegradation became effective after ten years. The slope of the mass ratio curve shown in Figure 5.5 increased in almost all cases provided highest biodegradation rate between ten and twenty years. Then the biodegradation decreased after twenty years. The contaminant mass reduction was about 97% by the end of fifty years. This Figure indicates that the contaminant plume migration is not much sensitive to changes in the dispersivities, $\alpha_L$ and $\alpha_T$. Changing dispersivities caused changes in plume longitudinal and transverse dispersion. In all simulated scenarios, 0.3 of contaminant mass ratio was remaining after twenty years except for scenario that has value of dispersivities 10 & 1, about 0.35 contaminant mass ratio left. However, after fifty years, all simulated scenarios resulted in the biodegradation of more than 0.9 contaminant mass ratio.
Figure 5.4: Effect of decreasing (a) and increasing (b) dispersivity on the biomass concentration after 40 years.
5.2 Sensitivity of Natural Attenuation to Changes in Contaminant Mass Flux

In this section, the effects of changes in mass flux (ML^{-2}T^{-1}) value on the contaminant concentration in both cases and the presence and the absence of the bacteria are examined. The contaminant mass flux is calculated as 2.3 mg/day as clarified in chapter four. Then other selected mass flux values of 5 (case 1), 15 (case 2), 30 (case 3) and 60 (case 4) were tested and the results were compared with those of the base case.

First, contaminant mass fluxes of 5 and 15 were simulated in the presence of bacteria. Figure 5.6a describes the effect of increasing the mass flux to almost two and six times of the base case on the contaminant contour. The effect of using mass fluxes of 5 and 15 on the contaminant contours started at earlier time in source and plume zones, more contaminant is introduced to these zones as compared to the base case. After twenty years, more significant changes are observed especially in the source zone, the contaminant undergoes biodegradation process, while some escaped to the plume zone (Figure 5.6a). At
the late time, most of the contaminant in the source zone was biodegraded and less mass escaped to the plume zone when using a mass flux of 15.

Higher mass flux values of 30 and 60 were used. It is observed that at earlier time, the contaminant in the source zone exposed to high biodegradation rate and less contaminant escaped to the plume zone. After twenty years, the resultant contaminant contour assures the effect of using high mass flux values in the source zone, while at late time most of the contaminant in the source zone disappeared (Figure 5.6b). From results in Figures 5.6a,b, it is observed that the outer contaminant contour line (10 ppm) reached a distance of 700 m along y-axis. This indicates the biodegradation is less sensitive to this parameter.

In the second case, mass flux values of 5 and 15 in the absence of bacteria were simulated. It is noticeable that higher mass flux (15) results in more contaminant that introduced to the plume zone since the earlier time (Figure 5.7a). The same was observed when mass flux was increased to 30 and 60 (Figure 5.7b). The outer contour line of 10 in the case of using a mass flux of 15 reached to a distance of 750 m along the y-axis after forty years (Figure 5.7a), while the same contour line exceeds 750 m when a mass flux of 60 mg/day was used (Figure 5.7b).
Figure 5.6: Effect of different flux values on contaminant concentration in the presence of bacteria.
the late time, most of the contaminant in the source zone was biodegraded and less mass escaped to the plume zone when using a mass flux of 15.

Higher mass flux values of 30 and 60 were used. It is observed that at earlier time, the contaminant in the source zone exposed to high biodegradation rate and less contaminant escaped to the plume zone. After twenty years, the resultant contaminant contour assures the effect of using high mass flux values in the source zone, while at late time most of the contaminant in the source zone disappeared (Figure 5.6b). From results in Figures 5.6a,b, it is observed that the outer contaminant contour line (10 ppm) reached a distance of 700 m along y-axis. This indicates the biodegradation is less sensitive to this parameter.

In the second case, mass flux values of 5 and 15 in the absence of bacteria were simulated. It is noticeable that higher mass flux (15) results in more contaminant that introduced to the plume zone since the earlier time (Figure 5.7a). The same was observed when mass flux was increased to 30 and 60 (Figure 5.7b). The outer contour line of 10 in the case of using a mass flux of 15 reached to a distance of 750 m along the y-axis after forty years (Figure 5.7a), while the same contour line exceeds 750 m when a mass flux of 60 mg/day was used (Figure 5.7b).
Figure 5.6: Effect of different flux values on contaminant concentration in the presence of bacteria.
Figure 5.7: Effect of different flux values on contaminant concentration in the absence of bacteria.
5.3 Sensitivity of Natural Attenuation to Changes in Bacterial Maximum Specific Growth Rate

METABIOTRANS is used to investigate the influence of increasing or decreasing the maximum growth rate $\mu_{\text{max}}$ (day$^{-1}$) on the contaminant concentration through four scenarios. It was assumed that $\mu_{\text{max}}$ has value of 0.005 day$^{-1}$ in the base case, the effects of increasing and decreasing $\mu_{\text{max}}$ by 25% and 50% of its base value were considered and the outputs were compared with the results of the base case. The contaminant contour lines for different values of $\mu_{\text{max}}$, 0.0025 (case 1) and 0.00125 (case 2) after ten, twenty and forty years are given in Figure 5.8a. It is clear that at earlier time, the two shown contour lines are almost identical. This means that the effect of decreasing $\mu_{\text{max}}$ values is not yet observed after ten years. However, differences in the contaminant concentration near plume core are noticed at a late time. After forty years, the $\mu_{\text{max}}$ value of 0.0025 caused some changes in the contaminant concentration near plume core and the leading edge as the effect of biodegradation process appeared. The lowest $\mu_{\text{max}}$ value of 0.000125 did not show significant changes in the expected plume after forty years (Figure 5.8a).

The value of $\mu_{\text{max}}$ is increased to two (case 3) and four (case 4) folds of the base case value (0.01 and 0.02). The effect of increasing $\mu_{\text{max}}$ on the expected plume core appeared at the earlier times, when $\mu_{\text{max}}$ value is 0.02, high biodegradation rate occurred near the source zone and some of the contaminant escaped to the plume zone (Figure 5.8b). At late times, the effect of increasing biodegradation rate in the plume core resulted in less contaminant concentration that escaped to the plume leading edge. It is noticed that in the source zone bacterial biodegradation was higher with $\mu_{\text{max}}$ value of 0.02 as compared to the base case.

The effect of decreasing $\mu_{\text{max}}$ to 0.005 and 0.00125 after the first ten years on the
Figure 5.8: Effect of decreasing (a) and increasing (b) $\mu_{\text{max}}$ on the contaminant concentration
biomass concentration is shown in Figure 5.9a. It is noticeable that decreasing $\mu_{\text{max}}$ value to its quarter value resulted in a slow biomass growth. However, in the case of using $\mu_{\text{max}}$ value of 0.0025, the bacterial growth increased. At the tailing edge, the bacteria growth started and resulted in low biomass growth. In the core, the bacterial concentration increased and as a result less contaminant escaped to the leading edge; thus less biomass concentration was simulated at the plume leading edge (Figure 5.9a).

The effect of increasing $\mu_{\text{max}}$ to two and four folds of the base case value on biomass contours is shown in Figure 5.9b. Increasing $\mu_{\text{max}}$ value to double caused the biomass concentration to increase in the core, while less contaminant escaped to plume leading edge. In the case of increasing $\mu_{\text{max}}$ value to 0.02, the bacteria growth was accelerated in the plume tailing edge and in the core after ten years as compared to the case of using $\mu_{\text{max}}$ equals 0.01 with less contaminant escaped to the leading edge resulting in low biomass concentration at that edge. This matches with the results discussed in Figure 5.8b.

After twenty years, the microbial growth rate was still slow when $\mu_{\text{max}}$ value was 0.00125. However, the bacterial growth rate increased in the plume core with some contaminant escaped to the plume zone when $\mu_{\text{max}}$ value was 0.0025 (Figure 5.10a). It is obvious that the biomass growth is higher in the base case as compared to the case of using $\mu_{\text{max}}$ value 50% less than base value (Figure 5.10a).

More bacterial spreading could be observed as $\mu_{\text{max}}$ value increased. The low bacterial concentration at the leading edge of the plume is due to the escaped contaminant which was less in the case of highest $\mu_{\text{max}}$ due to the higher bacteria growth at the core of the plume (Figure 5.10b).

After forty years, the differences in the biomass concentration in the case of decreasing $\mu_{\text{max}}$ became more evident. Very low bacterial growth is simulated when $\mu_{\text{max}}$
Figure 5.9: Effect of decreasing (a) and increasing (b) $\mu_{\text{max}}$ on the biomass concentration after 10 years.
Figure 5.10: Effect of decreasing (a) and increasing (b) $\mu_{\text{max}}$ on the biomass concentration after 20 years.
was 0.00125. The source zone exposed to bacterial growth, but again not enough to prevent contaminant migration (Figure 5.11a).

Figure 5.11b represents biomass growth in the case of using higher values of $\mu_{\text{max}}$ (0.01 and 0.02) which simulated more biodegradation as compared to the base case. Higher bacterial concentration is observed when $\mu_{\text{max}}$ value is increased. The bacterial concentration at the leading edge of the plume is becoming less after forty years (Figure 5.11b). This indicates the of higher biodegradation rate in the core of the plume; therefore less amount of the contaminant escaped especially in the case of the $\mu_{\text{max}}$ was 0.02.

The effect of changing $\mu_{\text{max}}$ on the ratio of contaminant mass in any simulation to contaminant mass of the second base case is represented in Figure 5.12. It is very clear that with higher values of $\mu_{\text{max}}$, higher bacterial growth rates are simulated and consequently more biodegradation occurs. It is observed that less than 50% of the contaminant mass was biodegraded after fifty years when $\mu_{\text{max}}$ value was reduced to its quarter. On the other hand, almost 98% of the contaminant mass was reduced when $\mu_{\text{max}}$ value was increased four times (Figure 5.12). The slope of the curve in Figure 5.12 represents over all biodegradation rate. Biodegradation rate in the case of $\mu_{\text{max}}$ equals 0.02 at earlier time was the highest, but decreases after twenty years and stabilizes until the end of the fifty years. On the other hand, biodegradation rate in the case of $\mu_{\text{max}}$ equals 0.0025 is almost zero in the first fifteen years, but increases biodegraded mass reaches 0.8 by the end of fifty years.
Figure 5.11: Effect of decreasing (a) and increasing (b) $\mu_{\text{max}}$ on the biomass concentration after 40 years.
5.4 Sensitivity of Natural Attenuation to Changes in Initial Biomass Concentration

In this section, the effect of increasing and decreasing initial biomass concentration, Mo (ML⁻³) on contaminant concentration are studied. Initial biomass concentration were decreased and increased to two and four folds and the results were compared with that of base case.

In order to investigate the sensitivity of the predicted contaminant concentration to the changes in initial value of M, three simulations were performed with Mo equals 0.001 (base case), 0.0005 (case 1) and 0.00025 (case 2). Figure 5.13a shows the contaminant contours for the three cases after ten years. Small changes are observed in the source zone when decreasing Mo to half and quarter of the base case value. However, noticeable difference is observed after twenty years in the source zone, more contaminant is observed in the plume core.
Figure 5.13: Effect of decreasing (a) and increasing (b) $Mo$ on the contaminant concentration.
After forty years, it is clear that the reactions in the source zone were fast enough to remediate the contaminant. It is noticed that as Mo decreased, the bacterial growth rate decreased and more contaminant escapes biodegradation (Figure 5.13a).

On the other hand, increasing Mo two and four folds caused increasing in the biodegradation when compared to the base case. Figure 5.13b shows that at earlier time the source zone of the contaminant is exposed to high bacterial growth, but it increased more after forty years especially in the source zone. However, some of the contaminant escaped to form a plume down stream. It is evident that with higher values of Mo, more contaminant is biodegraded.

The biomass contour in Figure 5.14a represents the simulation results after ten years. It assures that when the Mo decreased to 0.0005, less biomass concentration were produced as compared to the base case. Higher biomass concentrations are observed near source zone. When Mo value is further decreased to 0.00025, lower biomass concentration is produced. The low bacterial concentration at the tailing edge indicates low bacteria growth rate. The lowest bacteria concentration in the source zone is observed in the case of Mo value of 0.00025. This is because it takes longer time for the biodegradation reaction to begin and therefore less biomass is produced, and some of the contaminant escaped to the plume front leading edge.

The biomass contours after ten years in the case of increasing Mo value by 100% and 300% are displayed in Figure 5.14b. The biomass concentration in the base case is the lowest and the concentration is increased when the value of Mo was increased especially in the source zone. The highest biomass concentration in the source zone in the case of Mo equals 0.004 gives indication of high bacterial growth rate.

The biomass contours after twenty years in the cases of decreasing Mo to 0.0005 and 0.00025 are shown in (Figure 5.15a). Less biomass concentration in plume core is
Figure 5.14: Effect of decreasing (a) and increasing (b) Mo on the biomass concentration after 10 years.
Figure 5.15: Effect of decreasing (a) and increasing (b) Mo on the biomass concentration after 20 years.
produced with some contaminant escaped to the plume zone when Mo equals 0.00025 as compared to the case when Mo equals 0.0005.

Figure 5.15b represents the situation of increasing the value of Mo to 0.002 and 0.004. After twenty years, the concentration of bacteria increased more in the source zone due to high microbial growth rate when Mo equals 0.004. The increase of biomass concentration led to high contaminant biodegradation. However, less biomass is produced in the plume core when Mo equals 0.002 as compared to 0.004. As the initial biomass concentration increased, the biodegradation of the contaminant increased too.

The effect of decreasing the value of Mo to 0.0005 and 0.00025 on the biomass concentration after forty years is displayed in Figure 5.16a. Higher biomass concentration is observed in the plume core when Mo equals 0.0005 as compared to 0.00025. The bacterial growth at the plume tailing fringe was slow when Mo equals 0.00025, while it is higher when Mo equals 0.0005 with some contaminant escaped to the plume zone. The effects of increasing Mo value to two and four folds after forty years are shown in Figure 5.16b. The highest biomass concentration is produced in the case of highest value of Mo especially in the plume core. The bacterial growth was faster at the plume tailing edge when Mo equals 0.004 (Figure 5.16b).

In Figure 5.17, the changes in the contaminant mass with respect to time clarified the effect of the initial biomass concentration on the contaminant biodegradation rate. In the case of increasing Mo to the double (0.002), \( m/m_{o \text{ base case}} \) equals to approximately 0.3 by the end of twenty years. In the case of decreasing Mo to the half (0.0005) after twenty years, \( m/m_{o \text{ base case}} \) equals to approximately 0.45. The higher initial biomass concentration led to higher contaminant mass reduction. However, if the same situations were considered after forty years, the difference between the two ratios in these cases will be less than 0.1. This is because the overall biodegradation rate increases after ten years and
Figure 5.16: Effect of decreasing (a) and increasing (b) Mo on the biomass concentration after 40 years.
then decreases gradually after twenty years as shown in Figure 5.17.

5.5 Sensitivity of Natural Attenuation to Changes in Bacterial Decay Rate

The decay rate, $B$ (T$^{-1}$), is inversely proportional to the microbial growth rate as illustrated in modified Monod equation (equation 1.14). The effect of changing the microbial decay rate on biodegradation is investigated hereafter.

In most studies, the decay rate has a small value, almost equal to the zero; therefore, we choose the base case value of $B$ to be zero (Mohamed and Hatfield, 2005, Schafer, 2001). The first value is selected to be 0.1 of the growth rate ($\mu_{\text{max}}$) or 0.0005. Another two values of 0.000125 and 0.0005 were selected. Figure 5.18a shows the effects of using different values of $B$ on the contaminant contours. It is observed that after ten years no significant difference as compared with the base case has occurred (Figure 5.18a). However, this difference becomes evident after twenty years near the source zone, when high $B$ was simulated, less biodegradation occurred and more contaminant escaped to the plume zone. $B$ value of 0.0005 results in less biomass, as expected, and therefore, more
Figure 5.18: Effect of decreasing (a) and increasing (b) B on the contaminant concentration.
contaminant escaped to the plume zone. After forty years, the source zone is exposed to high biodegradation rate than the plume zone especially when $B$ equals 0. Higher biomass concentration was present when $B$ equals 0.000125; thus less contaminant escaped to the plume zone.

Figure 5.18b represents the simulation using $B$ equals 0.001 and 0.002. It is noticeable that the effect of changing $B$ value on the contaminant concentration started in the source zone at earlier time. The highest value of $B$ caused less concentration of biomass and as a result more contaminant escaped to form the plume which becomes clear after twenty years. After forty years, $B$ equals 0.002 showed no changes in the contaminant contour, most of the contaminant escaped to form the plume (Figure 5.18b).

The effect of the decay rate on the biomass contours at the earlier time is illustrated in Figure 5.19a. The rapid decay of the bacteria is simulated and caused the appearance of smaller biomass concentration in the case of $B$ equals 0.0005. In the case of using $B$ equals 0.000125, the biomass contour assures the accumulation of bacteria in the source zone, but less than that in the base case. The rapid bacterial decay when compared to the base case did not allow the bacteria to grow as compared to the base case (Figure 5.19a).

Figure 5.19b displays the biomass contour in the case of increasing $B$ to 0.001 and 0.002. The highest decay rate of bacteria (0.002) results in less biomass concentration with more contaminant escaped to plume zone. If the base case is compared with the case that has a $B$ equals 0.001, highest biodegradation rate especially in the source zone of the base case is observed (Figure 5.19b).

The biomass concentration in source zones increased after twenty years (Figure 5.20a). The density of the bacterial community in the core increased when $B$ equals 0.000125, but some of the contaminant escaped to the plume zone as the effect of decay rate appeared (Figure 5.20a). Less biomass accumulation can be observed in the plume
Figure 5.19: Effect of decreasing (a) and increasing (b) $B$ on the biomass concentration after 10 years.
Figure 5.20: Effect of decreasing (a) and increasing (b) B on the biomass concentration after 20 years.
core when $B$ equals 0.0005 due to the high bacterial decay rate.

The results of increasing $B$ to 0.001 and 0.002 after twenty years are shown in Figure 5.20b. Setting $B$ equals 0.002 resulted in minimum biomass concentration and therefore minimum biodegradation rate. In the case of $B$ equals 0.001, very low biomass concentration is observed in the plume core. This gives indication of slow biodegradation rate due to the effect of high bacterial decay rate (Figure 5.20b).

The observations in Figure 5.21a and b assures the inverse effect of using highest $B$ on the biodegradation process after forty years. Low biomass concentration in the case of using $B$ equals 0.001 is observed in the source zone and it decreased gradually toward the core (Figure 5.21b). The higher bacterial decay rate in case of $B$ equals 0.001 led to lower bacteria concentration and therefore more contaminant escaped to the plume zone. On the other hand, using $B$ equals 0.000125 which is almost ten times less than 0.001, resulted in higher biomass concentration in the source zone (Figure 5.21a). When $B$ was set to 0.0005, the concentration of bacteria was high at the beginning and then it decreased gradually and more contaminant escaped to the plume zone due to high bacterial decay rate after forty years (Figure 5.21a). At a late time, the simulated result of using $B$ equals 0.002 was the worst among the others. Very low biomass concentration in the source zone is observed (Figure 5.21b), while most of the contaminant escaped to the plume zone. This findings match with the results discussed in (Figure 5.18b).

The ratio between the contaminant mass and the initial mass of the base case with respect to time in the case of using $B$ equals 0.002 is identical to the base case (Figure 5.22). In the case of setting $B$ equals 0.000125, the biodegradation became effective at earlier time, while in the case of setting $B$ equals 0.001, the biodegradation started after ten years. The slope of the biodegraded mass in the case of $B$ equals 0.000125 was high between 10-20 years. Then it decreased gradually and resulted by the end of fifty years in a
Figure 5.21: Effect of decreasing (a) and increasing (b) $B$ on the biomass concentration after 40 years.
90% contaminant mass reduction. Using $B$ equals 0.0005 resulted in a 70% contaminant mass reduction after fifty years, while only 50% of contaminant mass is biodegraded in the case of $B$ equals 0.001. This indicates that, as expected, the lowest $B$ results in the highest contaminant mass reduction (Figure 5.22).

5.6 Sensitivity of Natural Attenuation to Changes in Half Saturation Constant

Half saturation constant, $K_s$ (ML$^{-3}$), is defined as substrate concentration when the maximum substrate reaction with microorganism equals to its half value. There is an inversely proportional relationship between $K_s$ and microbial growth rate as indicated in Monod equation (equation 1.14).

It is assumed that $K_s$ in the base case was set equal to 250. The effect of other $K_s$ values of 125 and 63 were investigated. Figure 5.23a shows the effect of using $K_s$ equals 63 and 125 on the contaminant concentration. It is noticed that decrease $K_s$ to 63 affected the contaminant concentration earlier in the source zone as compared to the case of $K_s$.
Figure 5.23: Effect of decreasing (a) and increasing (b) $K_s$ on the contaminant concentration.
equals 125. After twenty years, the effect of the using $K_s$ equals 125, becomes evident in both zones; source and plume. More biodegradation occurred and less contaminant escaped to the plume zone. At the late time, most of the contaminant contours disappeared especially with $K_s$ equals 63 in source and plume zones. However, more contaminant escaped in to the plume zone in the case of using $K_s$ equals 125 because of slow microbial growth as compared to the case of using $K_s$ equals 63. The smallest $K_s$ value led to high biomass growth rate.

$K_s$ is increased to two and four times folds in the next two simulations to be 500 and 1000. It is noticeable from Figure 5.23b that the effect of using $K_s$ of 500 and 1000 appeared slightly at earlier times in the source zone. After twenty years, both $K_s$ values of 500 and 1000 affected the contaminant contour adversely as compared to the base case as most of the contaminant escaped to the plume zone. The contaminant plume undergoes low biodegradation process after forty years compared to the base case in both $K_s$ simulation due to the presence of low bacteria (Figure 5.23b). Increasing $K_s$ ceased the biodegradation and allowed contaminant concentration to become high.

In Figure 5.24a, high biomass concentration in the source zone can be observed at earlier times when using $K_s$ of 63. $K_s$ represents the substrate concentration at which microorganism grow with half of maximum growth rate; that’s why when $K_s$ was increased to 125, low microorganisms growth is observed. The maximum biomass concentration in the base case is much less than that the other two cases (Figure 5.24a).

Figure 5.24b represents the biomass concentration in the cases of increasing $K_s$ two and four times of the base case value. It is very clear that the base case showed the highest biomass growth. The biomass concentration in the case of using a $K_s$ value of 500 is much less than that of the base case. The simulated biomass concentration when $K_s$ was set as 1000 shows lowest concentration. Lower microorganisms is simulated at tailing edge in the
Figure 5.24: Effect of decreasing (a) and increasing (b) $K_s$ on the biomass concentration after 10 years.
case of 500 is due to due to high $K_s$ value as compared to the base case. Low biomass concentration is observed when $K_s$ equals 1000, while high microbial growth is observed in the core.

The observations after twenty years in Figure 5.25a assure that using lowest value of $K_s$ enhanced the biodegradation process earlier. Using a $K_s$ value of 63 resulted in high concentration of the microorganism in the source zone, but still some of the contaminant escaped to the leading edge of the plume. The microbial growth in case of using $K_s$ of 125 was also higher than the base case (Figure 5.25a). It is noticed that the highest value of $K_s$ (1000) significantly reduces bacterial growth and; therefore, most of the contaminant escaped to the leading edge of the plume.

Figure 5.25b represents bacterial growth in the aquifer in the case of increasing $K_s$ to 500 and 1000 after twenty years. When $K_s$ was set equal to 1000, very low biomass concentration in the source zone is observed in Figure 5.25b; this is due to the presence of low microorganism in the region. However, high biomass concentration in the core is observed. In the case of using a $K_s$ value of 500, higher microbial accumulation in the core is observed as shown in Figure 2.25b. The high biomass concentration can be noticed in the plume core of the base case.

Figure 5.26a shows the effect of decreasing $K_s$ value to half and quarter of its original value after forty years. The simulated results when $K_s$ equals 63 and 125 show high biomass concentration in the core of these cases, but still the highest bacterial growth was observed when $K_s$ was set as 63, Figure 5.26a.

After forty years, the biomass concentration increased in the core when $K_s$ value of was increased to 1000. This might be due to the effects of the highest $K_s$ value on the biomass contour started after long time (Figure 5.26b). In the case of using $K_s$ value of 500, more bacteria accumulation in the core is observed. The effect of highest $K_s$ value
Figure 5.25: Effect of decreasing (a) and increasing (b) $K_s$ on the biomass concentration after 20 years.
Figure 5.26: Effect of decreasing (a) and increasing (b) $K_s$ on the biomass concentration after 40 years.
In Figure 5.27, the biodegradation in the case of using $K_s$ of 63 started earlier, while in the case of using $K_s$ of 1000 the effect of biodegradation on the contaminant mass started after twenty years. It is obvious that the lowest half substrate constant caused the highest contaminant biodegradation, almost 98% of the contaminant mass undergoes biodegradation after fifty years. When $K_s$ was 125, the contaminant biodegradation started earlier, but later than the case of $K_s$ equals 63. $K_s$ equals 125 results in almost 97% contaminant mass reduction by the end of fifty years (Figure 5.27). In the case of using $K_s$ of 500, biodegradation becomes effective after fifteen years, the slope of the reduced mass increased till forty years. When $K_s$ equals 500, almost 80% of contaminant mass biodegraded by the end of fifty years (Figure 5.27). When $K_s$ of 1000 was used, the slope of the reduced mass increased after twenty years, about 60% of the contaminant mass is reduced by the end of fifty years. This finding is compatible with results for Figure 5.26b.
5.7 Sensitivity of Natural Attenuation to Changes in Microbial Yield Coefficient

The microbial yield coefficient, $Y_s$, represents the biomass produced per unit mass of substrate biodegraded. The effects of the microbial yield factor and the accumulation of the biomass on the contaminant biodegradation in the subsurface are investigated in this section. There is an inverse relationship between biomass growth rate and the yield coefficient (equation 4.5).

The value of yield factor in the base case was assumed 0.01. Other values of 0.005 and 0.0025 were simulated and the results were compared with base case. Figure 5.28a clarifies that the contaminant contour exposed to little changes in the source zone after ten years when $Y_s$ was 0.0025. These changes become more evident in source and plume zones as the effect of biodegradation appeared after twenty years for both $Y_s$ values (0.005 and 0.0025). At the late time, most of the contaminant in the source zone was biodegraded and less contaminant escaped to the plume zone (Figure 5.28a).

Figure 5.28b represents the effects of increasing yield factors (0.02 and 0.04) on the contaminant contour. The contaminant contour exposed to little changes in the source zone. The effect of the using higher yield coefficient on both source and plume zones of the contaminant becomes clear at the late time. The highest yield factor (0.04) led to less contaminant biodegradation, however most of the contaminant in the source zone disappeared when $Y_s$ was set as 0.02 and 0.04 (Figure 5.28b). Higher yield factor led to less biomass growth and; therefore, less contaminant biodegradation.

The effect of the yield coefficient on the biomass concentration after ten years is shown in Figure 5.29a. It is obvious that using $Y_s$ of 0.005 and 0.0025 did not have a significant effect on the biomass concentration as compared to the base case at an earlier time. Also when the yield factor is increased to 0.02 and 0.04, no changes were observed as compared to the base (Figure 5.29b). It is noticeable that the maximum biomass
Figure 5.28: Effect of decreasing (a) and increasing (b) $Y_s$ on the contaminant concentration.
Figure 5.29: Effect of decreasing (a) and increasing (b) $Y_s$ on the biomass concentration after 10 years.
concentration in the cases of using $Y_s$ of 0.005, 0.0025, 0.02 and 0.04 is almost the same (Figures 5.26a and b).

After twenty years, differences in the biomass concentration become more evident (Figure 5.30a). The lowest yield factor (0.0025) produced the lowest biomass concentration in the source zone as shown in Figure 5.30a. In the base case, the bacterial growth was highest in the core, but some of the contaminant escaped to the plume zone (Figure 5.30a). When the highest yield coefficient (0.04) was used, high biomass concentration was observed especially in the core, while some of the contaminant escaped to leading edge of the plume (Figure 5.30b). Using $Y_s$ of 0.02 resulted in less biomass concentration especially in the tailing and leading edges of the plume.

In Figure 5.31a, setting $Y_s$ to 0.005 resulted in less microorganisms accumulation as compared to the base case. In the case of using $Y_s$ of 0.04, higher microbial growth is observed especially in the source zone after forty years, but some of the contaminant escaped the leading edge of the plume (Figure 5.31b).

Figure 5.32 shows the effect of the yield coefficient on the contaminant mass. In all simulations biodegradation started as early as five years, however the process started earlier when $Y_s$ was set to 0.0025. The slope of the mass ratio curve shown in Figure 5.32 decreased after twenty years in almost all cases provided contaminant mass reduction between 94%-96% by the end of fifty years. The least mass contaminant reduction produced after fifty years when $Y_s$ was 0.04. This Figure indicates that the contaminant plume migration is not much sensitive to changes in yield coefficient parameter, $Y_s$.

Based on the previous discussions, it is concluded that the contaminant plume migration is sensitive to changes in microbial growth rate and substrate half saturation constant parameters that showed significant effects on the biomass growth and consequently on the contaminant contours. On the other hand, the plume migration is less
Figure 5.30: Effect of decreasing (a) and increasing (b) $Y_s$ on the biomass concentration after 20 years.
Figure 5.31: Effect of decreasing (a) and increasing (b) $Y_s$ on the biomass concentration after 40 years.
Figure 5.32: The ratio of contaminant mass simulated with different $Y_s$ values to the contaminant mass of base case.

sensitive to changes in microbial decay rate and the initial microorganisms concentration. However, changes in microbial decay rate affected the biodegradation rate after ten years, while changes in initial biomass concentration affected contaminant mass biodegradation between ten and twenty years. Also, changes in microbial yield factor affected the biodegradation rate between ten and twenty years. The least sensitive parameter regarding contaminant biodegradation was the dispersivity.

In order to examine the effect of applying different biological and physical values on contaminant concentration at certain points, two points were selected. The first one is located near source zone and the other one is located at plume leading edge near the supply well. The first point has coordinates of $x$ equals 185 m and $y$ equals 300 m, while the second point (at plume leading edge) has coordinates of $x$ equals 120 m and $y$ equals 645 m. Contaminant concentrations were traced over fifty years.
Figure 5.33 shows the effect of using different $\mu_{\text{max}}$ values on contaminant concentrations near source zone (first point) over fifty years. It is very clear that $\mu_{\text{max}}$ equals 0.02 showed the minimum concentration peak, about 25 mg/l after ten years. As $\mu_{\text{max}}$ value decreased, the maximum concentration peak increased and shifted to the right side of peak as well as it became wide peak. This is because that the effect of the lowest value of $\mu_{\text{max}}$ parameter on contaminant concentration appears lately, the contaminant peak concentration was 250 mg/l approximately after thirty years.

Figure 5.34 shows half saturation constant impact on contaminant concentration at first point. The lowest $K_s$ value (63 mg/l) resulted in the lowest contaminant concentration peak. The effect of $K_s$ started earlier since the earlier time for all simulated values, however highest contaminant concentration (about 225 mg/l) was simulated using $k_s$ equals 1000 mg/l after 25 years. This indicates that the effect of $k_s$ on contaminant concentration was faster than $\mu_{\text{max}}$.

Figure 5.35 presented the effect of applying different Mo values on contaminant concentration at the first point. The minimum contaminant concentration was simulated using Mo value equals 0.004 mg/l. However, all simulated Mo values near source zone showed narrow and sharp contaminant concentration peak compared to that in the previous two parameters. The effect of all simulated Mo values appeared after ten years and ceased by the end of thirty years in contrast to the effect of $\mu_{\text{max}}$ and $K_s$. The difference between the minimum contaminant concentration (about 90 mg/l) simulated using Mo equals 0.004 mg/l and the maximum contaminant concentration (about 140 mg/l) simulated using Mo equals 0.00025 mg/l is 50 mg/l. This indicates that the effect of using different Mo values on contaminant concentration was less as compared to $\mu_{\text{max}}$ and $K_s$ where big contaminant concentration peak differences between different simulated values can be observed.
Figure 5.33: Contaminant concentration simulated with different $\mu_{\text{max}}$ values near source zone.

Figure 5.34: Contaminant concentration simulated with different $K_s$ values near source zone.
Figure 5.35: Contaminant concentration simulated with different Mo values near source zone.

Figure 5.36 shows the effect of using different B values on contaminant concentration near source zone. It is very clear that the contaminant concentrations when B equals 0.002 and in the case of bacteria absent are identical. The rapid bacterial decay rate led to existence of high contaminant concentration near source zone. The minimum contaminant concentration peak of about 100 mg/l was simulated in the base case (B equals 0). Increasing the bacterial decay factor led to the detection of highest contaminant concentration. The difference between the contaminant concentration peaks in the base case and when B equals 0.001 was about 125 mg/l. This indicates that B affected the contaminant concentration near source zone more than Mo. Also, most of the simulated B values resulted in broad peak as compared to that simulated with different Mo values.

Figure 5.37 presents the effect of different simulated Y_s values on contaminant concentration near source zone. All simulated Y_s started their effect on contaminant concentration after five years and ceased by the end of thirty years. The minimum contaminant concentration peak of about 80 mg/l was simulated when Y_s equals 0.0025.
Figure 5.36: Contaminant concentration simulated with different B values near source zone.

Figure 5.37: Contaminant concentration simulated with different Y₅ values near source zone.
after fifteen years. On the other hand, the maximum contaminant concentration peak of about 145 mg/l was detected when $Y_s$ equals 0.004 after eighteen years. This indicates that the effect of using different $Y_s$ on contaminant concentration were less as compared to $B$, $\mu_{\text{max}}$ and $K_s$.

Figure 5.38 shows the effect of using different contaminant mass flux on contaminant concentration near source zone. It is very clear that using contaminant mass flux of 2.3 mg/day resulted in broad peak with maximum value of about 100 mg/l of contaminant concentration. As the contaminant mass flux increased, the peak became sharp with increasing in contaminant concentration. The highest contaminant mass flux (60 mg/day) diffused more contaminant near source zone and resulted in more than 750 mg/l of contaminant concentration after ten years.

Figure 5.39 presents the contaminant concentration peaks simulated with different values of longitudinal and transverse dispersivities. All the simulated scenarios started after five years and ceased by the end of thirty years. All simulated scenarios have maximum contaminant concentration peaks at fifteen years with small differences in the maximum peak values. Increasing dispersivities led to changes in plume dispersion in longitudinal and transverse direction which resulted in less contaminant concentration as a whole. The highest contaminant concentration peak (105 mg/l) was simulated using $\alpha_L$ equals 1.25 and $\alpha_T$ equals 0.125.

The effect of using different $\mu_{\text{max}}$ values on contaminant concentration at leading plume edge (second point) is presented in Figure 5.40. All simulated scenarios started after thirty five years and most of figures were discontinued after fifty years which is the simulation time. The difference between the simulated values gives indication that the contaminant concentration is sensitive to changes in $\mu_{\text{max}}$ values. It is obvious that when $\mu_{\text{max}}$ equals 0.01, very small and broad peak was resulted due to low contaminant
Figure 5.38: Contaminant concentration simulated with different contaminant mass flux values near source zone.

Figure 5.39: Contaminant concentration simulated with different dispersivities values near source zone.
concentration left after fifty years. In the base case (0.005), the peak was bigger and sharper with highest contaminant concentration value equals 65 mg/l after forty five years.

Figure 5.41 shows the effect of different simulated $K_s$ value on contaminant concentration. When $K_s$ equals 63 mg/l, small contaminant concentration can be observed, but the peak was little bet sharper than that simulated using $\mu_{\text{max}}$ equals 0.02. This is because that $\mu_{\text{max}}$ affected contaminant concentration more than $K_s$. In the case of using $K_s$ equals 500 and 1000 mg/l, no peak can be observed after fifty years because of the end of simulation time. Increasing the base case two and four fold caused big changes in the simulated contaminant concentration at late time as compared to same scenarios near source zone.

Figure 5.42 shows the effect of $M_o$ parameter on contaminant concentration at leading plume edge. All simulated scenarios started their effect after thirty five years. The minimum contaminant concentration peak was detected when $M_o$ equals 0.004 mg/l after...
Figure 5.41: Contaminant concentration simulated with different $K_s$ values at plume leading edge.

Figure 5.42: Contaminant concentration simulated with different $M_o$ values at plume leading edge.
forty three years. However, maximum contaminant concentration peaks in the remaining
simulated scenarios was detected after forty five years with a difference of about 10 mg/l
between following two simulated scenarios. It is clear that using different values of Mo has
less effect on contaminant concentration as compared to $\mu_{\text{max}}$ and $K_x$.

Figure 5.43 shows the effect of using different $B$ values on contaminant
concentration at location farthest from source zone. As noticed before near source zone, $B$
equals 0.002 has similar effect as the case of bacteria absence on contaminant
concentration. The difference between the simulated contaminant concentrations in the
case of using $B$ equals 0.001 and 0.002 decreased at late time as compared to the same
cases near source zone. In the case of using $B$ equals 0.0005, discontinues in the simulated
contaminant concentration after fifty years and no peak was detected as compared to the
base case and when $B$ equals 0.000125.

Figure 5.44 shows the effect of using different $Y_s$ values on contaminant
concentration at plume leading edge over fifty years. All simulated scenarios resulted in
observed contaminant concentration peaks. The minimum contaminant concentration peak
of about 32 mg/l was detected when $Y_s$ equals 0.0025, while it was 62 mg/l approximately
in the base case. Increasing $Y_s$ value four times the base case led to small increment in the
contaminant concentration which was 85 mg/l approximately.

Figure 5.45 shows contaminant concentration simulated with different contaminant
mass flux at plume leading edge. Using contaminant mass flux of 60 mg/day caused
highest contaminant diffusion and therefore, highest contaminant concentration as
expected. The smallest and latest formed contaminant concentration peak was simulated
using contaminant mass flux of 2.3 mg/day.

Figure 5.46 shows the effect of longitudinal and transverse dispersivities on
contaminant concentration at plume leading edge. It is clear that using high dispersivities
Figure 5.43: Contaminant concentration simulated with different B values at plume leading edge.

---

Figure 5.44: Contaminant concentration simulated with different Y_s values at plume leading edge.
Figure 5.45: Contaminant concentration simulated with different contaminant mass flux values at plume leading edge.

Figure 5.46: Contaminant concentration simulated with different dispersivity values at plume leading edge.
values led to formation of smallest contaminant concentration similar to that observed near source zone. Decreasing the base case value dispersivities by 50%, led to highest contaminant concentration with sharp peak of value equals 72 mg/l after forty five years.
CHAPTER 6

ALTERNATIVES FOR REMEDIATION OF CONTAMINATION IN BU HASA FIELD
Chapter 6

Alternatives for Remediation of Contamination in Bu Hasa Field

The METABIOTRANS model is used in this chapter to present suitable remediation scenarios for groundwater contamination in the Liwa aquifer. The main objective is to minimize the concentration of the dissolved plume, resulted from the free phase hydrocarbon contamination that reaches the nearest supply well in the camp area.

In the biodegradation process, redox reaction is a process in which the oxidation of an electron donor is coupled with the reduction of an electron acceptor. In remediation scenarios, wells were used to inject the electron acceptor to stimulate redox reaction and therefore, enhance hydrocarbons remediation. Several numbers of wells were used in each scenario. Oxygen is selected as electron acceptor using solid or slow releasing oxygen source. The electron acceptor entered as constant flux and the initial condition is zero.

Remediation scenarios presented in this chapter are divided into four groups and absence of electron acceptor was assumed. In the first group, eight scenarios were simulated. Table 6.1 summarizes the difference among these scenarios. One well is placed at four different distances downstream from the center of source zone in scenarios one, three, five and seven. Two additional wells were placed 50 m from the center well and perpendicular to the flow direction in scenarios two, four, six and eight. Wells locations in group one are displayed in Figures 6.1a and b. The electron acceptor flux is assumed 50 mg/day/well for all cases as illustrated in Table 6.1.

In the second group, another eight scenarios were simulated. Table 6.2 illustrates the difference between scenarios of this group. These scenarios were built based on different combination of scenarios from group one to attain a maximum remediation (Table 7.2). Four wells are used in the first six scenarios in group two. The flux is kept as 50
Figure 6.1 (a) Wells locations in scenarios one, three, five and seven in group one  
(b) Wells locations in scenarios two, four, six and eight in group one  
(c) Wells locations in scenario sixteen

Figure 6.2: Electron acceptor contour lines (well at y distance of 200 m) in the absence of electron donor and bacteria.
mg/day/well in these scenarios. Five wells were used in each of the remaining two scenarios. In the last scenario all five wells were located near the source zone to maximize the intersected volume of electron acceptor by electron donor plume. The locations of wells in scenario sixteen are displayed in Figure 6.1c. Figure 6.2 shows the electron acceptor contours of scenario one in the absence of electron donor and bacteria.

The influence of applying different electron acceptor fluxes on the contaminant was studied in the scenarios of group 3 (Table 6.3). In the first three scenarios, one well at $y$ equals 200 m was used, with different electron acceptor fluxes. The next three scenarios have three wells with increased flux. Five wells were used in the last two scenarios with different electron acceptor fluxes of 100 and 200 mg/day/well. These five wells were 25 m apart normal to the flow direction with the center well located at $y$ equals 200 m.

Table 6.1 Remediation scenarios of group one

<table>
<thead>
<tr>
<th>Scenario No.</th>
<th>No. of wells</th>
<th>Location of wells in y-axis (m)</th>
<th>Flux/well (mg/day)</th>
<th>Total flux (mg/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>200</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>200</td>
<td>50</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>300</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>300</td>
<td>50</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>400</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>400</td>
<td>50</td>
<td>150</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>500</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>500</td>
<td>50</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 6.2 Remediation scenarios of group two

<table>
<thead>
<tr>
<th>Scenario No.</th>
<th>No. of wells</th>
<th>Combined scenarios</th>
<th>Location of wells in y-axis (m)</th>
<th>Flux/well (mg/day)</th>
<th>Total flux (mg/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>4</td>
<td>1 &amp; 4</td>
<td>1 at 200 &amp; 3 at 300</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>1 &amp; 8</td>
<td>1 at 200 &amp; 3 at 500</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>11</td>
<td>4</td>
<td>2 &amp; 3</td>
<td>3 at 200 &amp; 1 at 300</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>12</td>
<td>4</td>
<td>3 &amp; 8</td>
<td>1 at 300 &amp; 3 at 500</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>13</td>
<td>4</td>
<td>2 &amp; 7</td>
<td>3 at 200 &amp; 1 at 500</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>14</td>
<td>4</td>
<td>4 &amp; 7</td>
<td>3 at 300 &amp; 1 at 500</td>
<td>50</td>
<td>200</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>2 &amp; 4 (2 wells)</td>
<td>3 at 200 &amp; 2 at 300</td>
<td>50</td>
<td>250</td>
</tr>
<tr>
<td>16</td>
<td>5</td>
<td>1 &amp; 2 +1 well</td>
<td>5 at 200</td>
<td>50</td>
<td>250</td>
</tr>
</tbody>
</table>
The eight scenarios in the last group were selected based on the experience gained in the previous three groups with the ultimate objective of achieving maximum biodegradation (Table 6.4). In the first four scenarios, wells at y equal to 200 m and 400 m were used to treat the leading and the lateral fringes of the expected plume. However, it was found that more wells are needed to treat the leading edge of the plume and hence wells at y equal to 200 m, 300 m, 400 m and 500 m were placed in the last four scenarios.

Table 6.3: Remediation scenarios of group three

<table>
<thead>
<tr>
<th>Scenario No.</th>
<th>No. of wells</th>
<th>Location of wells in y-axis (m)</th>
<th>Flux/well (mg/day)</th>
<th>Total flux (mg/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>1</td>
<td>200</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>200</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>19</td>
<td>1</td>
<td>200</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>20</td>
<td>3</td>
<td>200</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>21</td>
<td>3</td>
<td>200</td>
<td>150</td>
<td>450</td>
</tr>
<tr>
<td>22</td>
<td>3</td>
<td>200</td>
<td>200</td>
<td>600</td>
</tr>
<tr>
<td>23</td>
<td>5</td>
<td>200</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>24</td>
<td>5</td>
<td>200</td>
<td>200</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 6.4: Remediation scenarios of group four

<table>
<thead>
<tr>
<th>Scenario No.</th>
<th>No. of wells</th>
<th>Location of wells in y-axis (m)</th>
<th>Flux/well (mg/day)</th>
<th>Total flux (mg/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>10</td>
<td>5 at 200 &amp; 5 at 400</td>
<td>150 &amp; 100</td>
<td>1250</td>
</tr>
<tr>
<td>27</td>
<td>10</td>
<td>5 at 200 &amp; 5 at 400</td>
<td>150 &amp; 200</td>
<td>1750</td>
</tr>
<tr>
<td>28</td>
<td>14</td>
<td>7 at 200 &amp; 7 at 400</td>
<td>150 &amp; 100</td>
<td>1750</td>
</tr>
<tr>
<td>29</td>
<td>14</td>
<td>7 at 200 &amp; 7 at 400</td>
<td>150 &amp; 200</td>
<td>2450</td>
</tr>
<tr>
<td>30</td>
<td>15</td>
<td>7 at 200 &amp; 5 at 300 &amp; 3 at 400</td>
<td>200 &amp; 200</td>
<td>3000</td>
</tr>
<tr>
<td>31</td>
<td>15</td>
<td>7 at 200 &amp; 3 at 300 &amp; 5 at 400</td>
<td>300 &amp; 300 &amp; 200</td>
<td>4200</td>
</tr>
<tr>
<td>32</td>
<td>17</td>
<td>7 at 200 &amp; 5 at 300 &amp; 5 at 400</td>
<td>200 &amp; 200 &amp; 200</td>
<td>3400</td>
</tr>
<tr>
<td>33</td>
<td>17</td>
<td>7 at 200 &amp; 7 at 400 &amp; 3 at 500</td>
<td>150 &amp; 200 &amp; 150</td>
<td>2900</td>
</tr>
</tbody>
</table>
6.1 Remediation Scenarios of Group One

Results of the remediation scenarios of group one assured that the locations of the wells played a vital role in contaminant degradation. One well was used in scenarios one, three, five and seven, while three wells were used in scenarios two, four, six and eight. In the first scenario, the well was located at a distance of 200 m along the y-axis, 90 m away from the center of the source zone.

Scenario one (Figure 6.3) shows that most of the contaminant plume core experienced high biodegradation rate for a distance of approximately 300 m. All the contaminant contour lines were displayed only after forty years. Using one well enhanced the biodegradation in the center of the expected plume, but did not affect the lateral fringes of the plume. The leading edge of the plume reached a distance of 700 m along the y-axis approximately.

In the second scenario, the number of wells was increased to three wells at a distance of 200 m along the y-axis maintaining the same flux for each well. Therefore, the total flux increased three times of that of the first scenario. The effect of the electron acceptor could be observed more clearly in the plume core and fringes. However, increasing the number of wells did not enhance the biodegradation at the leading edge. The outer contour line (10) reached to the same distance along the y-axis in both scenarios as shown in Figure 6.3. The leading edge was not exposed to enough biodegradation because there was no contact between electron acceptor and electron donor at this edge in both scenarios; one and two.

One well was located at a distance of 300 m along the y-axis in scenario three. Less amount of contaminant was biodegraded in the plume core as compared to scenario one. This is mainly because the contact volume between the electron acceptor and the electron donor was bigger in scenario one. The width of the biodegraded area in scenario three was
Figure 6.3: The contaminant concentration for remediation scenarios of group 1 after 40 years
smaller than that in scenario one which means that the lateral fringes were exposed to lower biodegradation rate in scenario three. Leading edge showed minor changes when compared to scenario one, Figure 6.3. Increasing number of wells in scenario four at the same distance along y-axis showed minor effects on biodegradation as compared to scenario three. The right fringe of the expected plume exposed to higher biodegradation rate than the left fringe, but less than that in scenario three. This may be due to the element size (5x5) that affected the symmetry of the expected plume as that the left and the right wells were not placed at exactly the same distance from the central well. This is because the nearest node to the proposed locations of the left and right wells were not placed at same distance from the central well. Because element size is 5x5, then the difference between the right and left distances is expected to be within ±2.5 m. This affected the symmetry of the simulated plume. The leading edge reached a distance of 700 m along the y-axis similar to the previous scenario.

It is clear that using wells far from the source zone will not led to better results. Scenario five and seven proves this (Figure 6.3), when one well was used at a distance of 400 m and 500 m along the y-axis. The plume core showed a minor change in scenario five, while in scenario seven this change almost null. The leading edges in scenarios five and seven reached to the same distance. The lateral fringes did not experience biodegradation in both scenarios.

Adding two more wells in scenario six caused minor changes in lateral fringes. The three wells at a distance of 500 m along y-axis in scenario eight had less effect on lateral fringes of the expected plume (Figure 6.3). Increasing number of wells in scenarios six and eight did not enhance biodegradation at the leading edges.

At earlier times, the electron acceptor contour lines for scenario one extended in the center than edges giving the chance for the interception of the contaminants (Figure 6.4).
Figure 6.4: The electron acceptor concentration in scenario 1.

Figure 6.5: The biomass growth in scenario 1.
The concentration of the electron acceptor in the center of the plume was higher than its fringes. Therefore, the contact between the electron acceptor and the contaminant was highest in the center. After forty years, the electron acceptor contours escaped the contaminant source zone to the front edge of the electron acceptor plume. Most of the plume core has been biodegraded, while the biodegradation at the leading edge of the plume was less. This is because that the intersection between electron acceptor, electron donor and the bacteria at the leading edge was less as compared to the source zone.

The results of biomass contours supported the previous results as clarified in Figure 6.5. At the earlier time, the bacteria growth was concentrated near the well location. After twenty years, the rate of bacteria growth increased in the area of electron acceptor injection. Less concentration of bacteria could be noticed in the right side of well location. After forty years, the bacteria accumulation near the well led to more contaminant biodegradation. However, some of the contaminant escaped to the plume leading edge which resulted in low bacteria concentration. The shape of the biomass color contours matched the biodegraded area in the contaminant contour lines. Using well near the source zone caused bacteria to grow and react with the hydrocarbon contaminant causing reduction in the contaminant concentration.

The effect of the electron acceptor on the contaminant mass of the different scenario is shown in (Figure 6.6). Scenario two showed the greatest contaminant biodegradation as more than half of the contaminant mass is reduced by the end of fifty years. Less than 50% of the contaminant mass was reduced in scenario one. On the other hand, scenario seven and eight showed the least reduction in contamination. Less than 10% of the contaminant were biodegraded after fifty years in scenarios seven and eight (Table 6.5). Scenario four resulted in contaminant mass reduction of 0.43 of the base case.

The biodegraded contaminant mass in scenario five was almost half of that in
scenario three, Figure 6.6. The slope of the reduced mass of scenarios one and two was steep between 25-35 years, while it was mild at the earlier time. At late times, the slope stabilized till 50 years.

The bioremediation efficiency can be calculated using the following equation:

$$\eta = [1 - (m/m_o)] \times 100$$  \hspace{1cm} (6.1)

where m is the contaminant mass in a specific scenario and m_o is contaminant mass in the base case.

Table 6.5: Bioremediation efficiency of group one.

<table>
<thead>
<tr>
<th>Scenario No.</th>
<th>Bioremediation efficiency ((\eta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>43</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
</tr>
</tbody>
</table>
6.2 Remediation Scenarios of Group Two

The remediation scenarios in group two are combinations of scenarios from group one. Scenario nine was the combination of scenario one and four (Table 6.2). The plume core biodegraded for approximately 250 m as clarified in Figure 6.8. The biodegraded area in scenario nine was less than that in scenario one. The right lateral fringe exposed to higher biodegradation rate than the left fringe due slight unsymmetry explained earlier. The leading edge reached a distance of about 700 m along the y-axis.

In scenario ten, Figure 6.7, the wells at a distance of 300 m along the y-axis were replaced by wells at a distance of 500 m along the same axis. It was observed that scenario ten has a similar effect as of scenario nine on the plume core biodegradation, but no changes in lateral fringes were observed. This means that the injected electron acceptor in the well at a distance of 200 m along the y-axis played a vital role in enhancing the biodegradation process. The wells at a distance of 300 m enhanced biodegradation more than the wells at a distance of 500 m along the same axis. In scenario nine, small changes could be noted in the leading edge as compared to scenario ten.

Increasing the number of wells at y equals 200 m in scenario eleven resulted in a contaminant plume similar to that in scenario two (Figure 6.7). This indicates that adding one well at y equal 300 m did not enhance biodegradation. In scenario twelve, improvements in the biodegradation process near the plume core were observed as compared to scenario eight. This is mainly because of the added well of scenario three. On the other hand, the lateral fringes and the leading edge were not affected (Figure 6.7).

Scenario thirteen resulted in almost the same changes in the plume of scenario eleven (Figure 6.7). However, the biodegraded area in the plume core in scenario thirteen was somehow less than that in scenario eleven. The intersection between the electron acceptor and the electron donor in scenario eleven was more than that in scenario thirteen.
Figure 6.7: The contaminant concentration for remediation scenarios of group 2 after 40 years.
This increased the biodegradation rate in the plume core. The wells at a distance of 200 m along the y-axis enhanced the biodegradation in the lateral fringes especially at the right side.

The observation in scenario fourteen (Figure 6.7), supported the previous findings; The well added at y equals 500 m did not enhance the biodegradation as compared with scenario four. The biodegraded areas in the plume core were almost similar. Adding one well at y equals 500 m did not increase the biodegradation at the leading edge of the plume.

The observations in the last two scenarios of group two indicated that using wells at a distance of 200 m along the y-axis is the key to increase the biodegradation rate. Scenario sixteen showed better results than scenario fifteen. Figure 6.7 shows that most of the plume core disappeared and further more the leading edge of the plume experienced a biodegradation.

The concentrations of the electron acceptor in scenario nine are higher compared to those in scenario one. However, in scenario nine, three more wells at a distance of 300 m along y-axis were used (Figure 6.8), there was no improvement in the plume core.

The biomass concentration at the earlier time are similar to that in scenario one as shown in Figure 6.9. In the first twenty years, high bacterial concentration is noted near the location of the well at a vertical distance of 200 m, but less biomass concentration was observed near the location of wells at a distance of 300 m. After forty years, the bacteria concentration near the locations of the wells at 300 m increased. However, no noticeable changes were observed in the contaminant contours. More biomass was accumulated in the plume core and led to high biodegradation rate as compared to its fringes.

In the first ten years, the reduction of the contaminant mass of all scenarios was almost zero. The slope of the reduced mass in most of the scenarios increased after twenty
Figure 6.8: The electron acceptor concentration in scenario 9.

Figure 6.9: The biomass concentration in scenario 9.
years (Figure 6.10). The effect of the electron acceptor on the contaminant mass of scenario nine is similar to that of scenario one (Figure 6.10). About 53% of the contaminant mass is biodegraded after fifty years. Scenarios ten and fourteen caused a contaminant mass reduction of about 40% (Table 6.6). Scenario sixteen resulted in a contaminant mass reduction of 71%, while 26% of the contaminant mass is removed in scenario twelve by the end of fifty years. It was also observed that scenario eleven, thirteen and fifteen were similar; matching previous finding discussed in Figure 6.7.

Table 6.6: Bioremediation efficiency of group two.

<table>
<thead>
<tr>
<th>Scenario No.</th>
<th>Bioremediation efficiency ($\eta$) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>53</td>
</tr>
<tr>
<td>10</td>
<td>42</td>
</tr>
<tr>
<td>11</td>
<td>66</td>
</tr>
<tr>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td>13</td>
<td>67</td>
</tr>
<tr>
<td>14</td>
<td>43</td>
</tr>
<tr>
<td>15</td>
<td>65</td>
</tr>
<tr>
<td>16</td>
<td>71</td>
</tr>
</tbody>
</table>
6.3 Remediation Scenarios of Group Three

Group three of the remediation scenarios studied the effect of applying different electron acceptor fluxes on the enhancement of contaminant biodegradation. All wells were put at y equals 200 m. In the first three scenarios, one well was used. The resultant contaminant contours indicated that the higher the applied electron flux, the more contaminant biodegradation will result especially in the plume core as observed in Figure 6.11. The width of the biodegraded area in scenario nineteen increased compared with scenario seventeen because of using high electron flux (400 mg/day), however the length of the biodegraded area was almost the same. Also, the width of the biodegraded area in scenario eighteen was little bet less than that in scenario nineteen because the electron acceptor flux in scenario nineteen is four times the electron acceptor flux in scenario eighteen.

The leading edges of the contaminant plume in all these scenarios were the same; no critical changes among them could be observed. The fringes of the expected plume were not affected and the leading edges reached to a distance of 700 m along the y-axis.

In the scenarios twenty, twenty one and twenty two, three wells were set. It seems that the center well is the most effective one as clarified in Figure 6.11. It was responsible for the biodegradation in the plume core, while the remaining two wells affected the plume fringes. The outer contour line (10 ppm) of the plume reached to a distance of 700 m along the y-axis in all three scenarios. The highest flux applied in scenario twenty two led to the highest biodegradation rate.

In the last two scenarios in group three, five wells were set at y equals 200 m. The results of these scenarios indicated that increasing the number of lateral wells do not enhance the biodegradation process even when applying a high electron acceptor flux (Figure 6.11). The concentration of electron acceptor in the lateral wells was less than that
Figure 6.11: The contaminant concentration for remediation scenarios of group 3 after 40 years.
Figure 6.11: The contaminant concentration for remediation scenarios of group 3 after 40 years (cont.)

Figure 6.12: The electron acceptor concentration in scenario 18.
in the center well. The width of the biodegraded area in all these scenarios was almost the same. These observations were contrary to that in the first three scenarios in group three as the width of the biodegraded area increased in the first three scenarios. This is may be due to the location of the well near the source zone. However, the inner contour line at plume leading edge (90 ppm) decreased in scenario twenty four compared to scenario twenty three. The outer contour line (10 ppm) of the expected plume in the last three scenarios of group three reached to a distance of 700 m along the y-axis.

The results of the electron acceptor contours of scenario eighteen confirmed that increasing the flux will activate the bacteria growth and therefore enhance the biodegradation process (Figure 6.12). It is noticeable that high concentration of the electron acceptor near the well location has led to the disappearance of most plume core contaminant. The electron acceptor in the front edge of the plume did not affect the contaminant because concentration of electron acceptor and electron donor were not high enough to stimulate bacteria.

Higher biomass concentration was observed in scenario eighteen after the first twenty years compared to scenario one (Figure 6.13). Also, after forty years, the maximum concentration of the biomass in scenario eighteen exceeded that in scenario one due to high electron acceptor flux. This resulted in increasing the width of the biodegraded area in scenario eighteen, while no changes were observed at the front edge of the plume (Figure 6.13).

The slope of all scenarios in group three at the earlier time was mild and it started to increase obviously after twenty years. It is obvious from Figure 6.14 that the contaminant mass reduced to about 50% by the end of fifty years in scenarios eighteen and nineteen. Table 6.7 shows that scenario seventeen produced least remediation in group three, 55% of the contaminant mass was left after fifty years. The effect of the electron
Figure 6.13: The biomass concentration in scenario 18.

Figure 6.14: The ratio of contaminant mass simulated in scenarios of group three to the contaminant mass of base case.
acceptor on the contaminant mass reduction was the highest in scenario twenty three and twenty four, 29% of the contaminant mass was left at late times (Table 6.7). The effect of increasing the flux value could also be observed in scenarios twenty two between 30-40 years, while the results of scenarios twenty and twenty one were almost identical. All scenarios result in a reduction of almost 45%-71% of the contaminant mass after fifty years (Figure 6.14). These results support the previous one regarding the contaminant concentration contour (Figure 6.11).

Table 6.7: Bioremediation efficiency of group three.

<table>
<thead>
<tr>
<th>Scenario No.</th>
<th>Bioremediation efficiency (η) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>45</td>
</tr>
<tr>
<td>18</td>
<td>54</td>
</tr>
<tr>
<td>19</td>
<td>56</td>
</tr>
<tr>
<td>20</td>
<td>64</td>
</tr>
<tr>
<td>21</td>
<td>63</td>
</tr>
<tr>
<td>22</td>
<td>63</td>
</tr>
<tr>
<td>23</td>
<td>71</td>
</tr>
<tr>
<td>24</td>
<td>71</td>
</tr>
</tbody>
</table>

6.4 Remediation Scenarios of Group Four

The last group consists of eight scenarios in which high numbers of wells was considered. Scenario twenty six showed noticeable improvements in the biodegradation process as compared to the previous groups (Figure 6.15). Most of the contaminant in the plume core and the plume fringes of both sides experienced high biodegradation rate. When the electron acceptor flux of the wells set at a “y” distance of 400 m, was increased to 200 mg/day as in scenario twenty seven, the inner contour in the leading plume zone disappeared. However, the plume fringes were not affected.
Figure 6.15: The contaminant concentration for remediation scenarios of group 4 after 40 years.
Increasing the number of wells as in scenario twenty eight, Figure 6.14 led to a splitting in the contaminant plume, but did not affect the leading plume zone as compared to scenario twenty six. The leading edges in these scenarios reached to a "y" distance of 700 m.

In scenario twenty nine, the flux of wells, set at the same distance along the y-direction, was increased as in scenario twenty seven. The entire contour of the plume zone experienced biodegradation, but the outer contaminant contour lines reached a distance of 700 m in the y-direction (Figure 6.15). It is obvious that increasing the number of wells at 200 m and 400 m along the y-axis caused splitting in the plume.

Increasing the total number of wells as in scenario thirty did not reduce the plume as compared to the previous four scenarios (Figure 6.15). This indicated that adding wells at a distance of 300 m along the y-direction did not activate the biodegradation process in the plume core. The leading plume edge was almost similar to that in scenario twenty eight. It reached a distance of 700 m along the y-axis. However, the splitting area decreased slightly.

In scenario thirty one, the electron acceptor fluxes were increased while keeping the total number of wells as fifteen. The result was not better than that of scenario thirty (Figure 6.15). The biodegradation process occurred in the plume core, while no splitting occurred in the fringes. Increasing the total fluxes did not cause retardation of the leading edge; it again reached a distance of 700 m along the y-direction after forty years.

In scenario thirty two, the flux per well was kept as 200 mg/day, but the total number of wells was increased. The resultant contaminant plume was similar to that in scenario thirty; therefore increasing the number of wells at a distance of 400 m along the y-axis did not enhance the biodegradation process in the plume core. The splitting occurred in the fringes due to the increase of the number of wells at a distance of 300 m in the y-
direction as compared to scenario thirty one. The leading plume edge reached a distance of 700 m along the y-direction and no changes were observed in the inner leading plume zone (Figure 6.15).

The results of scenario thirty three were similar to that of scenario twenty nine. Three wells were used at y equals 500 m but they did not activate the biodegradation process. The wells at 200 m and 400 m were sufficient to cause the biodegradation in the plume core and the splitting in its fringes. In all previous scenarios, the outer contaminant contour line of 10 ppm reached a distance of 700 m (Figure 6.15).

The high concentration of the electron acceptor contours in scenario twenty six explained the reason of the reduction in the contaminant contour since early time in both the plume core and its front fringe. Two separated electron acceptor plumes could be observed; one for each set of wells (Figure 6.16). After twenty years, the plume of the wells set at y equals 200 m reached the plume of the other set, while at the late time it appeared as one contour. The reason behind this is that most of the electron acceptor was consumed in the core of the electron donor plume (Figure 6.16).

The biomass contour in Figure 6.17 clarifies the idea that the bacteria growth at the centre well was the highest since the earlier time. However, bacterial concentrations at other wells increased after twenty years, but were still less than that of the center well. It is obvious that the bacteria growth near the wells at y equals 200 m (where the electron acceptor flux was 150 mg/day/well) was higher than that at y equals 400 m (where the flux was 100 mg/day/well). The wells at y equals 200 m led to the biodegradation of most of the plume core, while the wells at y equals 400 m enhanced the biodegradation rate at the front fringe.

The effect of the electron acceptor on the contaminant mass of the scenarios of group four showed no differences in the mass reduction among the eight scenarios as
Figure 6.16: The electron acceptor concentration in scenario 26.

Figure 6.17: The biomass concentration in scenario 26.
clarified in Figure 6.18. The slope of reduced mass increased after ten years and then decreased by the end of forty years. All the scenarios caused contaminant mass reduction between 73% and 76% after fifty years (Table 6.8). The high values of contaminant mass reduction compared to group three is because that the last group of scenarios resulted in contaminant biodegradation in both areas; plume core and plume leading zone.

From the previous results, it is concluded that the location of the well in the center of the plume plays an effective role in the biodegradation process at the plume core, whereas the wells on the sides have less effect. Also, the locations of the wells are very important; the nearest wells to source zone showed better results, while the farthest wells were not as effective as the central one. Plume splitting was observed only when the number of wells was increased to seven at y equals 200 m. increasing the flux may result in more reduction in the leading plume zone.
Table 6.8: Bioremediation efficiency of group four.

<table>
<thead>
<tr>
<th>Scenario No.</th>
<th>Bioremediation efficiency (η) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>73</td>
</tr>
<tr>
<td>27</td>
<td>74</td>
</tr>
<tr>
<td>28</td>
<td>75</td>
</tr>
<tr>
<td>29</td>
<td>76</td>
</tr>
<tr>
<td>30</td>
<td>74</td>
</tr>
<tr>
<td>31</td>
<td>73</td>
</tr>
<tr>
<td>32</td>
<td>74</td>
</tr>
<tr>
<td>33</td>
<td>76</td>
</tr>
</tbody>
</table>

The effect of selected remediation scenarios on contaminant concentration was examined at the same two points mentioned in chapter 5.

Figure 6.19 shows the effect of selected remediation scenarios from group one on contaminant concentration near source zone. In the base case which represents no injection, minimum contaminant concentration peak was detected. This is because abundant of electron acceptor was assumed. Scenario one has the second minimum contaminant concentration peak. The contaminant concentration simulated with scenario two did not show big difference as compared to scenario one. The contaminant concentration simulated with scenario three resulted in highest broad bandwidth peak with maximum value of 240 mg/l. Placing well at position farthest from source zone did not show decreasing in contaminant concentration as in scenario five which was identical to the case of bacteria absent.

Figure 6.20 presented contaminant concentration simulated with selected scenarios form group one, two and three. Scenario seven did not cause decreasing in contaminant concentration compared to the case of bacteria absent. Scenario sixteen showed maximum contaminant concentration value of 112 mg/l approximately. The maximum contaminant concentration peak simulated in the base case has a value of about 105 mg/l, which is less
Figure 6.19: Contaminant concentration simulated with selected scenarios of group one near source zone.

Figure 6.20: Contaminant concentration simulated with selected scenarios of groups one, two and three near source zone.
than scenario sixteen by less than 10 mg/l. Increasing electron acceptor flux of one well placed at 200 m resulted in decreasing contaminant concentration as in scenarios eighteen and nineteen when compared to scenario one. The maximum contaminant concentration peak simulated in scenarios eighteen and nineteen has a value of 90 mg/l, while it was in scenario one 140 mg/l. However, the contaminant concentration simulated with scenarios eighteen and nineteen were almost similar to the base case, small difference in maximum contaminant concentration value is observed.

Figure 6.21 shows contaminant concentration simulated with selected scenarios from group three and four. Increasing electron acceptor flux of more than two wells did not enhance the biodegradation as in scenarios twenty and twenty two. The simulated contaminant concentration in scenarios twenty and twenty two were almost similar, wide peak can be observed. The minimum contaminant concentration peak of value 110 mg/l was simulated in scenario twenty six with small difference with that in the base case.

Figure 6.22 presents contaminant concentration simulated with selected scenarios from group four near source zone. The contaminant concentration peaks simulated with scenarios twenty seven, twenty eight and twenty nine were identical, and no improvement in biodegradation resulted from increasing number of wells or increasing electron acceptor flux.

Figure 6.23 shows the differences in contaminant concentration simulated with selected scenarios of group one at plume leading edge. All simulated scenarios started their effect after thirty five years and maximum contaminant concentration peaks were detected after forty five years. The minimum contaminant concentration peak with a value of 60 mg/l simulated with the base case where abundant of electron acceptor was assumed. However, the maximum contaminant concentration peak with a value of 95 mg/l was simulated with scenario five.
Figure 6.21: Contaminant concentration simulated with selected scenarios of groups three and four near source zone.

Figure 6.22: Contaminant concentration simulated with selected scenarios of group four near source zone.
Figure 6.23: Contaminant concentration simulated with selected scenarios of group one at plume leading edge.

Figure 6.24 presents contaminant concentration simulated with selected scenarios from group one, two and three at location farthest from source zone. The simulated contaminant concentration peaks simulated with scenarios eighteen and nineteen were almost identical and have a value of 80 mg/l. Scenario seven did not show improvement in the contaminant concentration at plume leading edge.

Figure 6.25 shows contaminant concentration simulated with selected scenarios from group three and four at location farthest from source zone. Scenario twenty six shows less contaminant concentration than other two scenarios, because there are only three wells at 200 m simulated in scenario twenty and twenty two with different electron acceptor flux in each scenario. The effect of these scenarios was obvious near source zone than at plume leading edge, however, scenario twenty six has more five wells placed at 400 m.

Figure 6.26 presents contaminant concentration simulated with selected scenarios from group four at plume leading edge. The simulated contaminant concentration in
Figure 6.24: Contaminant concentration simulated with selected scenarios of groups one, two and three at plume leading edge.

Figure 6.25: Contaminant concentration simulated with selected scenarios of groups three and four at plume leading edge.
Figure 6.26: Contaminant concentration simulated with selected scenarios of group four at plume leading edge.

Scenarios twenty seven, twenty eight and twenty nine were identical.
CHAPTER 7
SUMMARY, CONCLUSIONS AND RECOMMENDATIONS
Chapter 7

Summary, Conclusions and Recommendations

7.1 Summary

Bu Hasa Liquid Recovery Plant receives associated gas from Abu Dhabi Company for Onshore Oil Operations (ADCO) through pipelines. The associated gas undergoes several processes to produce natural gas liquid (NGL). The waste liquid; mixture of water and hydrocarbons which result from this process is knocked out. The hydrocarbon is recovered as a natural gas liquid, while the residual water is treated and/or disposed off onsite which may constitute a source of groundwater contamination.

The groundwater reservoir in Bu Hasa field is composed of number of aquifers that extend to depth of 1,640 m below the ground surface. The unconfined Liwa aquifer is the shallowest one and is used as the main source of camp water supply in the area. This aquifer is the main focus of this thesis.

Since 1999, Abu Dhabi Industries Ltd. (Gasco) engaged companies to assess the extent of the hydrocarbon migration in the subsurface near the former warm blowdown area at Bu Hasa LRP. Matrix Solutions Inc. concluded that free and dissolved hydrocarbons are present in the subsurface. In 2005, URS Corporation signed a contract with Gasco to undertake groundwater remediation at the site. In this area, URS estimated the volume of free phase hydrocarbon as 10,225 m³. The presence of free phase hydrocarbons on the top of the water table is a source of groundwater contamination. The partial dissolution of the dissolved constituents has resulted in the formation of the dissolved hydrocarbon plume. Matrix Solutions Inc. reported the presence of dissolved benzene in at least one monitoring well.

In this thesis, a study is conducted to evaluate the potential of various remediation scenarios to reduce the concentration of the dissolved hydrocarbon reaching the production
wells in the camp area of Bu Hasa I.R.P. The study was conducted using the 3-D finite element model (METABIOTRANS).

Chapter one is an introduction and presents the transport equations that explain the different physical, chemical and biological contaminant transport processes in the subsurface. These processes include diffusion, advection, dispersion, adsorption, volatilization and biodegradation. Different physical, chemical and biological remediation technologies of NAPLs contaminant are discussed in this chapter. In chapter two, a literature review of some latest studies on remediation of groundwater contaminanted with NAPLs is presented. A description of Bu Hasa field and the production process of natural gas are presented in chapter three. A discussion of NAPLs contamination incident in the subsurface of Liwa aquifer is also presented in this chapter. Chapter four gives a description and limitation of METABIOTRANS model including the governing equations solved by the model. The geological and chemical information of the Liwa aquifer are presented in chapter four. This chapter presents model domain description as well as the hydrogeological and biological parameters. Initial and boundary conditions are also defined in this chapter. A sensitivity analysis study of the dissolved contaminant plume migration to changes in several physical, chemical and biological parameters is presented in chapter five. Chapter six presents the potential of different remediation scenarios in minimizing the contaminant concentration that reaches the nearest production well in the camp area of Bu Hasa field.

7.2 Conclusions

A sensitivity analysis study was performed to investigate the sensitivity of the dissolved plume migration to changes in several parameters in chapter five. The microbial growth rate and substrate half saturation constant have the dominate effects on the contaminant plume migration. The microbial decay rate and the initial biomass
concentration are less effective on the contaminant plume migration. The effects of microbial yield factor, dispersivities and the contaminant mass flux—within the assumed range—are the lowest.

The highest value of $\mu_{\text{max}}$ (0.02 day$^{-1}$) results in the highest bacterial growth and consequently more biodegradation. About 98% of the contaminant mass is reduced after fifty years. However, when $\mu_{\text{max}}$ was set equal to 0.00125 day$^{-1}$, less than 40% of the contaminant mass is reduced by the end of fifty years.

All simulations using different values of the initial biomass concentration ($M_o$) values resulted in 94%-96% contaminant mass reduction after fifty years; showing that biodegradation is less sensitive to this parameter in the assumed range of values.

Using different values of microbial decay rate ($B$) resulted in noticeable changes in contaminant mass reduction than $M_o$. The result of the contaminant mass reduction when $B$ was equal to 0.002 showed that the biodegradation contaminant mass is the same as in the base case; which means that no biodegradation occurred. However, when $B$ was equal to 0.002 the produced biomass concentration after forty years was much less than that of the base case.

The effect of the half saturation constant ($K_s$) was evident even at earlier times. The lowest value of $K_s$ (63 mg/l) showed high biodegradation rate especially in the source zone and hence less contaminant escaped to the leading edge of the plume. It resulted in a 98% reduction of contaminant mass by the end of fifty years, while the highest $K_s$ value (1000 mg/l) resulted in only 60% contaminant mass reduction.

The microbial yield factor ($Y_s$) did not show noticeable changes on the biomass concentration at earlier times for all used values. All the simulated $Y_s$ values resulted in 94%-96% reduction of contaminant mass at late times; showing that biodegradation difference among simulated scenarios decreased after twenty years.
Increasing contaminant mass flux caused more contaminant to be introduced to the plume. The outer contour line (10 ppm) of the contaminant plume in almost all simulated flux scenarios reached 700 m along y-axis after forty years in the presence of bacteria. However, considering biodegradation resulted in lower contaminant concentration that escaped to the leading edge of the plume than the simulated cases in the absence of bacteria. This indicates that plume migration is less sensitive to the contaminant mass flux parameter.

Increasing or decreasing the plume dispersivity caused the least effect on the natural attenuation of the contaminant. All simulated results of contaminant mass reduction using different dispersivities values show 96-97% of biodegraded contaminant mass by the end of fifty years indicating that the biodegradation is much less sensitive to the dispersivity parameter.

Another study was performed in this thesis to enhance biodegradation of the contaminant. Several remediation scenarios were performed. Electron acceptors injected from different wells at different locations were examined. The effect of number and location of wells as well as the electron acceptor injection rate on the bioremediation is studied in chapter six. Results of the remediation scenarios assured that the location of the well is an important factor in the biodegradation process. The highest biodegradation rate occurs always at the central well where the highest contaminant concentrations exist. The nearest well to the source zone helps to stimulate bacterial growth for longer time and therefore, increases the biomass concentration. Increasing the number of lateral wells enhances the biodegradation at the lateral fringes.

Remediation scenarios in this study were separated into four groups. In group one scenarios, one well was placed at different distances from the center of the source, namely: 200 m, 300 m, 400 m and 500 m, while the injected electron acceptor flux per well was
kept as 50 mg/day. Then, the number of lateral wells was increased to three wells and the
electron acceptor flux was 50 mg/day/well. In group two, the first six scenarios have four
wells placed at different locations with respect to y-axis. Total electron acceptor flux for
these scenarios was 200 mg/day. The last two scenarios in group two have five lateral
wells with electron acceptor flux of 50 mg/day/well. In scenario sixteen, all five lateral
wells were placed at 700 m along y-axis. In group three, eight scenarios were simulated;
the following scenarios have the same number of wells, but they were different in the
injected electron acceptor flux per well. The remediation scenarios in group four were
selected based on the results gained from the previous groups. More wells were simulated
with total electron acceptor fluxes ranged between 1250 and 4200 mg/day.

The results of the contaminant mass reduction of group one show that when three
wells were used at y equals 200 m is the best remediation scenario; 66% of the mass is
reduced by the end of fifty years. The location of the wells near the source zone helps in
stimulating the bacterial growth.

The results of group two clarify that adding wells at farthest distance from the
source zone may enhance the biodegradation at the leading edge, but will not cause much
contaminant mass reduction. Among the scenarios of group two, scenario sixteen in which
five wells were used at y equals 200 m resulted in 71% contaminant mass reduction at a
late time, both the core plume and the leading edge experienced biodegradation. Scenarios
thirteen and fifteen achieved above 60% of contaminant mass reduction by the end of fifty
years. In scenario thirteen, four wells were used; three of them located at y equals 200 m,
while one well located at y equals 500 m. Five wells were used in scenario fifteen, three
wells located at y equals 200 m and two at 300 m.

Although increasing well flux of electron acceptor is expected to enhance the
biodegradation; scenarios of group three show no significant improvement in the
kept as 50 mg/day. Then, the number of lateral wells was increased to three wells and the electron acceptor flux was 50 mg/day/well. In group two, the first six scenarios have four wells placed at different locations with respect to y-axis. Total electron acceptor flux for these scenarios was 200 mg/day. The last two scenarios in group two have five lateral wells with electron acceptor flux of 50 mg/day/well. In scenario sixteen, all five lateral wells were placed at 700 m along y-axis. In group three, eight scenarios were simulated; the following scenarios have the same number of wells, but they were different in the injected electron acceptor flux per well. The remediation scenarios in group four were selected based on the results gained from the previous groups. More wells were simulated with total electron acceptor fluxes ranged between 1250 and 4200 mg/day.

The results of the contaminant mass reduction of group one show that when three wells were used at y equals 200 m is the best remediation scenario; 66% of the mass is reduced by the end of fifty years. The location of the wells near the source zone helps in stimulating the bacterial growth.

The results of group two clarify that adding wells at farthest distance from the source zone may enhance the biodegradation at the leading edge, but will not cause much contaminant mass reduction. Among the scenarios of group two, scenario sixteen in which five wells were used at y equals 200 m resulted in 71% contaminant mass reduction at a late time, both the core plume and the leading edge experienced biodegradation. Scenarios thirteen and fifteen achieved above 60% of contaminant mass reduction by the end of fifty years. In scenario thirteen, four wells were used; three of them located at y equals 200 m, while one well located at y equals 500 m. Five wells were used in scenario fifteen, three wells located at y equals 200 m and two at 300 m.

Although increasing well flux of electron acceptor is expected to enhance the biodegradation; scenarios of group three show no significant improvement in the

176
Figure 6.15: The contaminant concentration for remediation scenarios of group 4 after 40 years.
Increasing the number of wells as in scenario twenty eight, Figure 6.14 led to a splitting in the contaminant plume, but did not affect the leading plume zone as compared to scenario twenty six. The leading edges in these scenarios reached to a “y” distance of 700 m.

In scenario twenty nine, the flux of wells, set at the same distance along the y-direction, was increased as in scenario twenty seven. The entire contour of the plume zone experienced biodegradation, but the outer contaminant contour lines reached a distance of 700 m in the y-direction (Figure 6.15). It is obvious that increasing the number of wells at 200 m and 400 m along the y-axis caused splitting in the plume.

Increasing the total number of wells as in scenario thirty did not reduce the plume as compared to the previous four scenarios (Figure 6.15). This indicated that adding wells at a distance of 300 m along the y-direction did not activate the biodegradation process in the plume core. The leading plume edge was almost similar to that in scenario twenty eight. It reached a distance of 700 m along the y-axis. However, the splitting area decreased slightly.

In scenario thirty one, the electron acceptor fluxes were increased while keeping the total number of wells as fifteen. The result was not better than that of scenario thirty (Figure 6.15). The biodegradation process occurred in the plume core, while no splitting occurred in the fringes. Increasing the total fluxes did not cause retardation of the leading edge; it again reached a distance of 700 m along the y-direction after forty years.

In scenario thirty two, the flux per well was kept as 200 mg/day, but the total number of wells was increased. The resultant contaminant plume was similar to that in scenario thirty; therefore increasing the number of wells at a distance of 400 m along the y-axis did not enhance the biodegradation process in the plume core. The splitting occurred in the fringes due to the increase of the number of wells at a distance of 300 m in the y-
direction as compared to scenario thirty one. The leading plume edge reached a distance of 700 m along the y-direction and no changes were observed in the inner leading plume zone (Figure 6.15).

The results of scenario thirty three were similar to that of scenario twenty nine. Three wells were used at y equals 500 m but they did not activate the biodegradation process. The wells at 200 m and 400 m were sufficient to cause the biodegradation in the plume core and the splitting in its fringes. In all previous scenarios, the outer contaminant contour line of 10 ppm reached a distance of 700 m (Figure 6.15).

The high concentration of the electron acceptor contours in scenario twenty six explained the reason of the reduction in the contaminant contour since early time in both the plume core and its front fringe. Two separated electron acceptor plumes could be observed; one for each set of wells (Figure 6.16). After twenty years, the plume of the wells set at y equals 200 m reached the plume of the other set, while at the late time it appeared as one contour. The reason behind this is that most of the electron acceptor was consumed in the core of the electron donor plume (Figure 6.16).

The biomass contour in Figure 6.17 clarifies the idea that the bacteria growth at the centre well was the highest since the earlier time. However, bacterial concentrations at other wells increased after twenty years, but were still less than that of the center well. It is obvious that the bacteria growth near the wells at y equals 200 m (where the electron acceptor flux was 150 mg/day/well) was higher than that at y equals 400 m (where the flux was 100 mg/day/well). The wells at y equals 200 m led to the biodegradation of most of the plume core, while the wells at y equals 400 m enhanced the biodegradation rate at the front fringe.

The effect of the electron acceptor on the contaminant mass of the scenarios of group four showed no differences in the mass reduction among the eight scenarios as
Figure 6.16: The electron acceptor concentration in scenario 26.

Figure 6.17: The biomass concentration in scenario 26.
clarified in Figure 6.18. The slope of reduced mass increased after ten years and then decreased by the end of forty years. All the scenarios caused contaminant mass reduction between 73% and 76% after fifty years (Table 6.8). The high values of contaminant mass reduction compared to group three is because that the last group of scenarios resulted in contaminant biodegradation in both areas; plume core and plume leading zone.

From the previous results, it is concluded that the location of the well in the center of the plume plays an effective role in the biodegradation process at the plume core, whereas the wells on the sides have less effect. Also, the locations of the wells are very important; the nearest wells to source zone showed better results, while the farthest wells were not as effective as the central one. Plume splitting was observed only when the number of wells was increased to seven at y equals 200 m. increasing the flux may result in more reduction in the leading plume zone.
Table 6.8: Bioremediation efficiency of group four.

<table>
<thead>
<tr>
<th>Scenario No.</th>
<th>Bioremediation efficiency ((\eta)) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>73</td>
</tr>
<tr>
<td>27</td>
<td>74</td>
</tr>
<tr>
<td>28</td>
<td>75</td>
</tr>
<tr>
<td>29</td>
<td>76</td>
</tr>
<tr>
<td>30</td>
<td>74</td>
</tr>
<tr>
<td>31</td>
<td>73</td>
</tr>
<tr>
<td>32</td>
<td>74</td>
</tr>
<tr>
<td>33</td>
<td>76</td>
</tr>
</tbody>
</table>

The effect of selected remediation scenarios on contaminant concentration was examined at the same two points mentioned in chapter 5.

Figure 6.19 shows the effect of selected remediation scenarios from group one on contaminant concentration near source zone. In the base case which represents no injection, minimum contaminant concentration peak was detected. This is because abundant of electron acceptor was assumed. Scenario one has the second minimum contaminant concentration peak. The contaminant concentration simulated with scenario two did not show big difference as compared to scenario one. The contaminant concentration simulated with scenario three resulted in highest broad bandwidth peak with maximum value of 240 mg/l. Placing well at position farthest from source zone did not show decreasing in contaminant concentration as in scenario five which was identical to the case of bacteria absent.

Figure 6.20 presented contaminant concentration simulated with selected scenarios form group one, two and three. Scenario seven did not cause decreasing in contaminant concentration compared to the case of bacteria absent. Scenario sixteen showed maximum contaminant concentration value of 112 mg/l approximately. The maximum contaminant concentration peak simulated in the base case has a value of about 105 mg/l, which is less
Figure 6.19: Contaminant concentration simulated with selected scenarios of group one near source zone.

Figure 6.20: Contaminant concentration simulated with selected scenarios of groups one, two and three near source zone.
than scenario sixteen by less than 10 mg/l. Increasing electron acceptor flux of one well placed at 200 m resulted in decreasing contaminant concentration as in scenarios eighteen and nineteen when compared to scenario one. The maximum contaminant concentration peak simulated in scenarios eighteen and nineteen has a value of 90 mg/l, while it was in scenario one 140 mg/l. However, the contaminant concentration simulated with scenarios eighteen and nineteen were almost similar to the base case, small difference in maximum contaminant concentration value is observed.

Figure 6.21 shows contaminant concentration simulated with selected scenarios from group three and four. Increasing electron acceptor flux of more than two wells did not enhance the biodegradation as in scenarios twenty and twenty two. The simulated contaminant concentration in scenarios twenty and twenty two were almost similar, wide peak can be observed. The minimum contaminant concentration peak of value 110 mg/l was simulated in scenario twenty six with small difference with that in the base case.

Figure 6.22 presents contaminant concentration simulated with selected scenarios from group four near source zone. The contaminant concentration peaks simulated with scenarios twenty seven, twenty eight and twenty nine were identical, and no improvement in biodegradation resulted from increasing number of wells or increasing electron acceptor flux.

Figure 6.23 shows the differences in contaminant concentration simulated with selected scenarios of group one at plume leading edge. All simulated scenarios started their effect after thirty five years and maximum contaminant concentration peaks were detected after forty five years. The minimum contaminant concentration peak with a value of 60 mg/l simulated with the base case where abundant of electron acceptor was assumed. However, the maximum contaminant concentration peak with a value of 95 mg/l was simulated with scenario five.
Figure 6.21: Contaminant concentration simulated with selected scenarios of groups three and four near source zone.

Figure 6.22: Contaminant concentration simulated with selected scenarios of group four near source zone.
Figure 6.23: Contaminant concentration simulated with selected scenarios of group one at plume leading edge.

Figure 6.24 presents contaminant concentration simulated with selected scenarios from group one, two and three at location farthest from source zone. The simulated contaminant concentration peaks simulated with scenarios eighteen and nineteen were almost identical and has a value of 80 mg/l. Scenario seven did not show improvement in the contaminant concentration at plume leading edge.

Figure 6.25 shows contaminant concentration simulated with selected scenarios from group three and four at location farthest from source zone. Scenario twenty six shows less contaminant concentration than other two scenarios, because there are only three wells at 200 m simulated in scenario twenty and twenty two with different electron acceptor flux in each scenario. The effect of these scenarios was obvious near source zone than at plume leading edge, however, scenario twenty six has more five wells placed at 400 m.

Figure 6.26 presents contaminant concentration simulated with selected scenarios from group four at plume leading edge. The simulated contaminant concentration in
Figure 6.24: Contaminant concentration simulated with selected scenarios of groups one, two and three at plume leading edge.

Figure 6.25: Contaminant concentration simulated with selected scenarios of groups three and four at plume leading edge.
scenarios twenty seven, twenty eight and twenty nine were identical.
CHAPTER 7

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS
Chapter 7
Summary, Conclusions and Recommendations

7.1 Summary

Bu Hasa Liquid Recovery Plant receives associated gas from Abu Dhabi Company for Onshore Oil Operations (ADCO) through pipelines. The associated gas undergoes several processes to produce natural gas liquid (NGL). The waste liquid; mixture of water and hydrocarbons which result from this process is knocked out. The hydrocarbon is recovered as a natural gas liquid, while the residual water is treated and/or disposed off onsite which may constitute a source of groundwater contamination.

The groundwater reservoir in Bu Hasa field is composed of number of aquifers that extend to depth of 1,640 m below the ground surface. The unconfined Liwa aquifer is the shallowest one and is used as the main source of camp water supply in the area. This aquifer is the main focus of this thesis.

Since 1999, Abu Dhabi Industries Ltd. (Gasco) engaged companies to assess the extent of the hydrocarbons migration in the subsurface near the former warm blowdown area at Bu Hasa LRP. Matrix Solutions Inc. concluded that free and dissolved hydrocarbons are present in the subsurface. In 2005, URS Corporation signed a contract with Gasco to undertake groundwater remediation at the site. In this area, URS estimated the volume of free phase hydrocarbon as 10,225 m$^3$. The presence of free phase hydrocarbons on the top of the water table is a source of groundwater contamination. The partial dissolution of the dissolved constituents has resulted in the formation of the dissolved hydrocarbon plume. Matrix Solutions Inc. reported the presence of dissolved benzene in at least one monitoring well.

In this thesis, a study is conducted to evaluate the potential of various remediation scenarios to reduce the concentration of the dissolved hydrocarbon reaching the production
wells in the camp area of Bu Hasa LRP. The study was conducted using the 3-D finite element model (METABIOTRANS).

Chapter one is an introduction and presents the transport equations that explain the different physical, chemical and biological contaminant transport processes in the subsurface. These processes include diffusion, advection, dispersion, adsorption, volatilization and biodegradation. Different physical, chemical and biological remediation technologies of NAPLs contaminant are discussed in this chapter. In chapter two, a literature review of some latest studies on remediation of groundwater contaminated with NAPLs is presented. A description of Bu Hasa field and the production process of natural gas are presented in chapter three. A discussion of NAPLs contamination incident in the subsurface of Liwa aquifer is also presented in this chapter. Chapter four gives a description and limitation of METABIOTRANS model including the governing equations solved by the model. The geological and chemical information of the Liwa aquifer are presented in chapter four. This chapter presents model domain descritization as well as the hydrogeological and biological parameters. Initial and boundary conditions are also defined in this chapter. A sensitivity analysis study of the dissolved contaminant plume migration to changes in several physical, chemical and biological parameters is presented in chapter five. Chapter six presents the potential of different remediation scenarios in minimizing the contaminant concentration that reaches the nearest production well in the camp area of Bu Hasa field.

7.2 Conclusions

A sensitivity analysis study was performed to investigate the sensitivity of the dissolved plume migration to changes in several parameters in chapter five. The microbial growth rate and substrate half saturation constant have the dominate effects on the contaminant plume migration. The microbial decay rate and the initial biomass
concentration are less effective on the contaminant plume migration. The effects of microbial yield factor, dispersivities and the contaminant mass flux—within the assumed range—are the lowest.

The highest value of $\mu_{\text{max}}$ (0.02 day$^{-1}$) results in the highest bacterial growth and consequently more biodegradation. About 98% of the contaminant mass is reduced after fifty years. However, when $\mu_{\text{max}}$ was set equal to 0.00125 day$^{-1}$, less than 40% of the contaminant mass is reduced by the end of fifty years.

All simulations using different values of the initial biomass concentration ($M_o$) values resulted in 94%-96% contaminant mass reduction after fifty years; showing that biodegradation is less sensitive to this parameter in the assumed range of values.

Using different values of microbial decay rate ($B$) resulted in noticeable changes in contaminant mass reduction than $M_o$. The result of the contaminant mass reduction when $B$ was equal to 0.002 showed that the biodegradation contaminant mass is the same as in the base case; which means that no biodegradation occurred. However, when $B$ was equal to 0.002 the produced biomass concentration after forty years was much less than that of the base case.

The effect of the half saturation constant ($K_s$) was evident even at earlier times. The lowest value of $K_s$ (63 mg/l) showed high biodegradation rate especially in the source zone and hence less contaminant escaped to the leading edge of the plume. It resulted in a 98% reduction of contaminant mass by the end of fifty years, while the highest $K_s$ value (1000 mg/l) resulted in only 60% contaminant mass reduction.

The microbial yield factor ($Y_s$) did not show noticeable changes on the biomass concentration at earlier times for all used values. All the simulated $Y_s$ values resulted in 94%-96% reduction of contaminant mass at late times; showing that biodegradation difference among simulated scenarios decreased after twenty years.
Increasing contaminant mass flux caused more contaminant to be introduced to the plume. The outer contour line (10 ppm) of the contaminant plume in almost all simulated flux scenarios reached 700 m along y-axis after forty years in the presence of bacteria. However, considering biodegradation resulted in lower contaminant concentration that escaped to the leading edge of the plume than the simulated cases in the absence of bacteria. This indicates that plume migration is less sensitive to the contaminant mass flux parameter.

Increasing or decreasing the plume dispersivity caused the least effect on the natural attenuation of the contaminant. All simulated results of contaminant mass reduction using different dispersivities values show 96-97% of biodegraded contaminant mass by the end of fifty years indicating that the biodegradation is much less sensitive to the dispersivity parameter.

Another study was performed in this thesis to enhance biodegradation of the contaminant. Several remediation scenarios were performed. Electron acceptors injected from different wells at different locations were examined. The effect of number and location of wells as well as the electron acceptor injection rate on the bioremediation is studied in chapter six. Results of the remediation scenarios assured that the location of the well is an important factor in the biodegradation process. The highest biodegradation rate occurs always at the central well where the highest contaminant concentrations exist. The nearest well to the source zone helps to stimulate bacterial growth for longer time and therefore, increases the biomass concentration. Increasing the number of lateral wells enhances the biodegradation at the lateral fringes.

Remediation scenarios in this study were separated into four groups. In group one scenarios, one well was placed at different distances from the center of the source, namely; 200 m, 300 m, 400 m and 500 m, while the injected electron acceptor flux per well was
kept as 50 mg/day. Then, the number of lateral wells was increased to three wells and the
electron acceptor flux was 50 mg/day/well. In group two, the first six scenarios have four
wells placed at different locations with respect to y-axis. Total electron acceptor flux for
these scenarios was 200 mg/day. The last two scenarios in group two have five lateral
wells with electron acceptor flux of 50 mg/day/well. In scenario sixteen, all five lateral
wells were placed at 700 m along y-axis. In group three, eight scenarios were simulated;
the following scenarios have the same number of wells, but they were different in the
injected electron acceptor flux per well. The remediation scenarios in group four were
selected based on the results gained from the previous groups. More wells were simulated
with total electron acceptor fluxes ranged between 1250 and 4200 mg/day.

The results of the contaminant mass reduction of group one show that when three
wells were used at y equals 200 m is the best remediation scenario; 66% of the mass is
reduced by the end of fifty years. The location of the wells near the source zone helps in
stimulating the bacterial growth.

The results of group two clarify that adding wells at farthest distance from the
source zone may enhance the biodegradation at the leading edge, but will not cause much
contaminant mass reduction. Among the scenarios of group two, scenario sixteen in which
five wells were used at y equals 200 m resulted in 71% contaminant mass reduction at a
late time, both the core plume and the leading edge experienced biodegradation. Scenarios
thirteen and fifteen achieved above 60% of contaminant mass reduction by the end of fifty
years. In scenario thirteen, four wells were used; three of them located at y equals 200 m,
while one well located at y equals 500 m. Five wells were used in scenario fifteen, three
wells located at y equals 200 m and two at 300 m.

Although increasing well flux of electron acceptor is expected to enhance the
biodegradation; scenarios of group three show no significant improvement in the
contaminant mass reduction when compared to the previous groups. The reduction in the contaminant mass of group three scenarios ranged between 45%-71% after fifty years.

A splitting of the contaminant plume was observed only when seven wells were located laterally near the source zone. The results of the scenarios of group four show almost similar contaminant mass reduction by the end of fifty years; about 73%-76% of contaminant mass is reduced. This indicates that increasing total number of wells and therefore, increasing total electron acceptor flux does not increase the biodegradation rate. Therefore, scenario twenty six in which has less number of wells (10 wells) is suggested.

7.3 Recommendations

This study presented a simulation of dissolved benzene plume migration in the subsurface of Liwa aquifer in Bu Hasa LRP. The results of sensitivity analysis of natural attenuation to changes in microbial growth rate indicated that increasing μmax value led to highest contaminant mass reduction (98%). Therefore, monitoring the natural attenuation in the field is not enough for contaminant degradation. It is recommended to enhance bioremediation possibly by adding certain microbial culture as it results in less hazardous products as compared to other chemical remediation techniques. Remediation scenarios in the saturated zone were suggested to reduce the risk of reaching high benzene concentration in the nearest supply well in the camp area of Bu Hasa field. The results of the remediation scenarios show that scenario twenty six in which ten wells were used; five wells located at y equals 200 m and the other five at 400 m has the greatest contaminant mass reduction. It results in the biodegradation of 73% of benzene mass after fifty years with less total number of wells and low electron acceptor flux as compared to scenarios twenty nine in which fourteen wells were used, seven wells located at y equals 200 m and the rest at 400 m, and thirty three in which seventeen wells were used, seven wells at y equals 200 m, and other seven wells at 400 m, and the remaining three wells located at y
equals 500 m. Also, it is concluded that placing wells near the source zone (at 200 m along y-axis) helps in increasing the biomass concentration and therefore, high biodegradation rate occurs and less benzene escapes to the leading edge of the plume and low contaminant concentration can be detected at nearest supplying wells in the camp area of Bu Hasa field.

Laboratory experiments based on field parameters and conditions besides numerical modeling can help in understanding the processes and predict the worst scenario before the contamination problem exacerbate. It is suggested that the dual efforts of field work and numerical simulation can minimize the risks and help in the decision making. Using benzene to trace groundwater contaminated with hydrocarbons is common in most of the studies as it is partially soluble in water as compared to other NAPLs compounds. However, it is recommended to consider toluene, ethylbenzen and xylene (TEX) compounds as they are harmful to human beings. It is also recommended to study the effect of the individual component of NAPLs to assess its risk and quantify it maximum concentration and compare the result with the permissible standard values.
References


GASCO. 2006. New oily water separator report (process water drum), Bu Hasa NGL unit. 01-25.


URS Corporation. 2005. Results of pre-remediation investigation report-Bu Hasa Refinery, UAE.
URS Corporation. 2006. Product recovery well installation in the redundant warm blowdown area report, Gasco-Bu Hașa facility. 01-04.


APPENDIX A
Appendix A: Physical Technologies

Air Sparging and Hydrogen Injection

This technique is based on the idea of introducing bubbles into the groundwater by pushing air into sparge wells or trenches under pressure, later on the volatile organics from the dissolved contaminant or that adsorbed to soil could be flushed out. The forced air would enhance the in situ bioremediation by adding oxygen to water or induce the movement of the contaminated water toward extraction wells.

When the vapour phase of contaminant reaches the unsaturated zone by the act of bubbles, vapour extraction system could be helpful in the treatment process as shown in Figure A.1. It is observed that air sparging technique is more effective in eliminating the dissolved hydrocarbons contaminant plume than treating the contaminant source. This technique is operated at high flow rate to maintain the contact between the groundwater, soil, and groundwater strip.

The chlorinated solvent contamination in groundwater could be treated using hydrogen which can be introduced to the subsurface in different ways such as the electrolysis, the injection of chemicals and dissolved in groundwater pump and reinjection process. The hydrogen acts as electron donor that controls the dechlorination process of the biological microorganism (Bedient et al., 1990).

Bioslurping

Bioslurping is an effective technique for simultaneously LNAPL recovery from water table and enhancing the bioremediation in the vadose zone. Bioslurping system consists of a well in which adjustable length of slurp tube is installed to reach LNAPL layer, the slurp tube is connected to vacuum system (Figure A.2). When pumping starts to remove LNAPL; the low pressure in the well emphasises the movement of LNAPL toward the well along with the LNAPL trapped in pores above the water table as shown in
Figure A.1: Process diagram for air sparging (Source: Bedient et al., 1990).

Figure A.2 Bioslurping system (Source: Motsch et al., 2002).
The slurp tube is drawn into extract vapour when the depression in the LNAPL layer occurs; the extraction of the vapour enhances the air influx to the vadose zone. Hence, the bioremediation of the unsaturated zone is promoted. The recovered LNAPL is then separated from the groundwater and soil vapor, LNAPL may be recycled, while the groundwater and soil vapor are discharged after treatment (Place et al., 2003).

**Dynamic Underground Stripping with Hydrous Pyrolysis Oxidation**

The dynamic underground stripping (DUS) is composed of steam injection, electrical resistance heating and underground imaging and monitoring techniques to mobilize and recover the contaminant in the subsurface. It is used in conjugation with hydrous pyrolysis oxidation (HPO) and is used for the destruction process of the remaining contaminant by the residual heat and the available oxygen.

The injection of steam and oxygen simultaneously results in the formation of heated oxygenated zone in the subsurface, when the injection is ceased; the steam condenses and the contaminated groundwater returns in the heated zone. The contaminated groundwater mixes with the oxygen and the heated condensate leading to the destruction of the dissolved contaminant. Thermophiles microorganisms are activated and natural biodegradation of certain contaminant will carry out.

The electric current is used to heat the contaminant trapped in the impermeable soil. It forces the vapour to the steam zone for further extraction as clarified in Figure A.3. (Motsch et al., 2002).

**Skimming**

This technique is based on using floating filter that has oleophilic/ hydrophobic mesh of high affinity to non polar compounds. The cylinder mesh in the recovery well is positioned floating on the LNAPL layer. The floated LNAPL on the water surface passes
Figure A.3: Dynamic underground stripping with hydrous pyrolysis oxidation (Source: Motsch et al., 2002).

Figure A.4: Skimming technique (Source: Motsch et al., 2002).
through the mesh, while water is rejected as shown in Figure A.4. The non aqueous phase is then collected in the central holding tanks on the surface after discharging it by air pressure. The pressure rate is controlled by timer; low and high level switches. The shallow well that has low rate of recovery can use belt of skimmer which string through LNAPL layer and up through pair of compression rollers. These rollers enhance the motivation force for the belt while squeezing out any retained LNAPL into container. The retained LNAPL is then pumped to the holding tank (Motsch et al., 2002).

**Soil Vapor Extraction System (SVE)**

The purpose of this technique is to get rid of volatile contaminants in the unsaturated zone. Most of the organic compounds are characterized by its high volatility when compared to its solubility. The partition of these organic compounds into the gas phase could be evaluated using vapor pressure and Henry’s law constant. The idea of this technique is to diffuse air through the contaminated soil, and then the extracted gas is either discharged to the atmosphere or entered to emission control device.

The contaminants that could be treated using SVE technique include gasoline and organic solvents that have volatile components. The efficiency of the treatment technique increases in high permeability soil within short time and can be evaluated by mass transfer rate of the contaminant from its aqueous phase into vapor phase. The advantages of SVE are the small disturbance effect on the soil, cost effective and build up of standard equipments.

Choosing SVE as a remediation technique requires two main important factors to be considered; properties of the contaminant such as the volatility, boiling point, solubility, octanol/water partition coefficient; and properties of the site such as permeability, organic carbon fraction and the moisture where air moves easily in drier soil.
SVE system has one or more extraction wells which should penetrate the unsaturated zone and extend to the capillary fringe. However, the wells are placed laterally in the case of shallow groundwater or where contaminants are encountered near the soil surface. The system contains one or more air inlet or injection wells to control pushing the air into different depths. Vacuum pumps or air blowers are used in the system to decrease the gas pressure in the extraction wells and increase the airflow to the wells. Flow meters are used to measure the extracted air volume and the vacuum gauges and indicate the total pressure lost in the system. Sampling ports are located at the head of each well, at the blower and after vapor treatment. In order to measure the concentrations of the soil vapor and the influenced vacuum radius in the extraction wells; vapor and pressure probes are used. An airflow pattern resulted from simple vapor extraction system is illustrated in Figure A.5.

It is found that SVE technique is more effective in treating water contaminated with trichloroethen, trichloroethane, tetrachloroethene and most of gasoline compounds. In the case of trichlorobenzene, acetone and heavier petroleum fuel, SVE shows less efficiency in removing them. A coupled techniques of SVE and pump and treat system could be effective in treating site contaminated with LNAPLs that residue on the water table. Using the pump system causes depletion in water table level leaving some of the LNAPLs sorbed on soil particles in the unsaturated zone which could be treated using SVE (Master, 1997).

**Pump and Treat Systems (PAT)**

Pump and treat system depends on the extraction of the contaminated groundwater and then undergoes treatment process on the surface (Figure A.6). The treated water could be injected into the aquifer or used for other purposes. However, the extraction of the contaminated groundwater does not mean that the contamination has been removed totally from the subsurface. The efficiency of the pumping process depends on the
Figure A.5: Simple vapor extraction system (Source: Bedient et al., 1990).

Figure A.6: Pump and treatment system (Source: EPA 542-R-01-021b, 2001).
characterization of the contaminant, the hydrological and the geological conditions of the field, and the efficiency of the pumping and the extraction design (Figure A.6).

Pump and treat systems may be designed to achieve two purposes; prevent spreading contaminant and restoration of groundwater by removing contaminant mass. The system is designed to reduce the spread of the contaminant; the rate of the extraction is maintained to avoid contaminant extension. On the other hand, if the system is designed to remove the contaminant mass, the rate of pumping clean water is maintained to flush the contaminated region which requires increasing its rate. The cost of a system designed for controlling contaminant is usually less than that of restoration system.

In order to design a system for groundwater pump and treat, four steps should be followed. The first step is defining the problem, which requires identifying the geology of the field and the hydraulic parameters and determining the contaminants of interest. The second step is screening the options of treatment technologies, which requires evaluation of the techniques in term of its availability and the total costs including the capital, the operation and the maintenance costs. The third step is the treatment system engineering which has two phases, process engineering phase and mechanical and electrical engineering phase. The first phase starts with the definition of the problem and screening the options of the treatment technologies and end with the selection of a specific process from a specific supplier. The second phase requires information on the requirement of the operation on specific site and the associated difficulties. The fourth step is the permitting step regarding the discharge of treated waste and emission to atmosphere (Suthersan, 1997).

**Permeable Reactive Subsurface Barrier (PRB)**

The basic concept of using a barrier is to restrict the contaminant plume movement in groundwater. A permeable reactive barrier in the subsurface is constructed of reactive
materials to intercept contaminant plume and allow it to flow through the reactive materials. When the contaminants in water pass through the barrier, it will be transferred into less harmful compounds or stationary species, so that it achieves the goal of groundwater remediation without restricting its flow.

Reactive materials should be suitable for the environment of the subsurface. They should not cause harmful chemical reaction or produce byproducts as a result of its reaction with contaminant constituents and should not be a source of contamination. It should not be from high soluble or depleted materials. Low to moderate cost materials are preferred. In order to perform a smoothly groundwater flow, reactive materials should not have too much small size particles or contain a varied particle sizes which may be blocked.

Iron metal Fe (0) (zero valent) iron is widely used as reactive material in PRB in the case of halogenated hydrocarbons contaminants. It acts as a reducing agent and enhances the dehalogenation process such as transferring trichloroethene into ethene. Also it is used as a reducing agent in oxyanions compounds and enhances the precipitation such as converting Cr (VI) oxides into non soluble hydroxide Cr (III). However, in the case of sulfate and nitrate contaminants, organic materials are used as reactive media to treat these contaminants biologically.

There are two basic configurations of PRBs; continuous PRBs and funnel and gate system. The continuous PRBs (Figure A.7) has minimum effect on groundwater flow patterns. In continuous PRB, a trench is excavated and backfilled with the reactive material. It does not need funnels, so that groundwater flow velocity is not affected. To achieve the goal of the constructed PRB, the cross sectional area of the contaminant plume should be covered by choosing suitable barrier area and its thickness should be sufficient for remediation purposes. Also, it is important to avoid underflow of the contaminated
Figure A.7: Plume capture by continuous PRB trenched system (Source: Puls et al., 1998).

Figure A.8: Plume capture by a funnel and gate system (Source: Puls et al., 1998).
groundwater by insuring that the hydraulic conductivity of the aquifer is less than that of PRB and PRB base should reach the impermeable zone.

Funnel and gate configuration (Figure A.8) require low permeability funnels that govern groundwater flow into the treatment gate. The funnels are either sheet pilings, slurry walls or other impermeable layer such as clay and bedrock. In contrast to continuous PRB, funnel and gate systems cause increasing the groundwater flow velocity to increase within the gate when compared to the natural gradient velocity as illustrated in Figure A.8. The permeable gate must have reactive media that have permeability equivalent or higher than that of the aquifer and its thickness should be suitable to insure fully contaminant remediation (Puls et al., 1998)
ملخص الدراسة

يعد تسرب المواد الهيدروكربونية إلى خزانات المياه الجوفية مشكلة خطيرة وواسعة الانتشار. لوحظ في عام 2000 وجود بعض المواد الهيدروكربونية في خزان ليوا للمياه الجوفية في منطقة حقل أبو حمصا لمعالجة السوائل. يعد خزان ليوا من خزانات المياه الجوفية الضحلة، ويمثل المورد الرئيسي للمياه في منطقة المعسكر التابعة للحقل. تم إعداد هذه الدراسة لمحاكاة تصرف البنزين المذاب (أحد هذه المواد الهيدروكربونية) في خزان ليوا للمياه الجوفية باستخدام النموذج الرياضي METABIONTRANS. لقد تمت محاكاة العمليات التي تتحكم في انتقال الملوث الذائب وهي الحمل، الانتشار، الامتصاص والتحلل بالبكتيريا. الهدف الرئيسي من هذه الرسالة هو منع أو ضمان وصول تركيز منخفض من الملوث المذاب في المياه الجوفية لخزان ليوا لأقرب بدور تابع للمعسكر. تم إعداد دراسة تحليلية لتحديد مدى حساسية انتقال الملوث المذاب للتغير في بعض الخصائص الطبيعية للخزان الجوفي والخصائص الكيميائية للملوث والخصائص البيولوجية للبكتيريا الموجودة بالخزان الجوفي. نتائج هذه الدراسة أظهرت أن هجارة الملوث المذاب أكثر تأثرًا بمعدل النمو البكتيري وثابت نصف الإشباع للملوث، بينما أقل تأثرًا بالتركيز الانتدائي للبكتيريا ومعدل ضمحلاتها. كما أظهرت الدراسة أن تأثر انتقال الملوث المذاب قليل الحساسية لمقابل التحصيل البكتيري، ومعامل الانتشار للخزان الجوفي والتدفق الكتلي للملوث. تم عمل عدة سناريوهات لمعالجة الملوث لتحقيق الهدف من هذه الرسالة وهو منع أو ضمان وصول تركيز منخفض من الملوث للمياه البنير القريبة من مصدر التلوث. عدة آثار استخدمت في ضخ مواد محفزة لتحسين عملية المعالجة للملوث. أكانت النتائج ارتفاع معدل النمو البكتيري بالقرب من البنير المركزي المستخدم في عملية المعالجة حيث توجد أعلى تركيز للملوث. وذلك لأن وجود البنير بالقرب من مصدر الملوث يحفز النمو البكتيري لفترة طويلة، وبالتالي فإن زيادة معدل تدفق المواد المحفزة يسرع النمو البكتيري.
عنوان الأطروحة:

نموذج إنتقال الملوثات الهيدروكربونية في خزان المياه الحوفي بمنطقة حقل أبو حصا وتقييم البدائل لمعالجتها

الاسم:
نوال عيسي صالح الجنبي

المشرف:
د. محمد مصطفى محمد قسم الهندسة المدنية و البيئية كلية الهندسة- جامعة الإمارات العربية المتحدة

مشرف مساعد:
أ.د. محسن شريف قسم الهندسة المدنية و البيئية كلية الهندسة- جامعة الإمارات العربية المتحدة
نمذجة إنتقال الملوثات الهيدروكربونية في خزان المياه الجوفي بمنطقة حقل أبوحصا وتقييم البدائل لمعالجتها

رسالة مقدمة لاستكمال متطلبات الحصول على درجة الماجستير في برنامج علوم موارد المياه

نوال عيسى صالح جنيبي

بكالوريوس العلوم (2000) جامعة الإمارات العربية المتحدة

01 ديسمبر 2008