

**GEO-ENVIRONMENTAL ASSESSMENT AND REMEDIATION
OF CONTAMINATED SITES: A CASE STUDY OF BARUWA
COMMUNITY, LAGOS, NIGERIA.**

BY

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DEDICATION

This thesis is dedicated to all my tutors and mentors who gave me the opportunity to be an academic.

ABSTRACT

The relationship between hydraulic, chemical and geotechnical properties is of crucial importance for the transport and fate of contaminants in the subsurface (porous media).

This research presents a methodology for physical laboratory aquifer modeling, field studies and development of a numerical solute transport model, for the simulation of the laboratory and field experiments. Three-dimensional (3D) sand tank (1.8 m x 0.3 m x 0.8 m) experiments were conducted to study contaminant transport and natural attenuation within the sand tank. The model was used to study the transport of an inorganic tracer (Chloride) and petroleum hydrocarbon in groundwater, within a tropical aquifer (porous media) material. The research has resulted in the designing and testing of the laboratory aquifer model (3-D sand tank) for subsurface contamination assessment and remediation techniques evaluation. This facility is now available at the Geotechnical Engineering Laboratory, Federal University of Technology, Akure.

Detailed geotechnical, hydraulic and geochemical characterization of the chosen laboratory experimental porous media material (Owena sand) and the field site subsurface soil were performed. This will provide basic experimental data on porous media materials, which would be widely useful to geotechnical/environmental researchers and engineers who are involved in contaminated site assessment and remediation in Nigeria. The Owena sand is a poorly graded sand (SP) with 88.1% Sand and 11.9% Gravel. Relevant geotechnical properties of the sand are; Coefficient of uniformity $C_u = 2.53$, coefficient of curvature $C_z = 0.181$, Hydraulic conductivity $K = 5.76 \times 10^{-4}$ m/s, Bulk density $\rho = 1.9$ Mg/m³, Effective Porosity $n_e = 0.215$ and Median grain diameter $D_{50} = 0.55$ mm. Other relevant hydraulic and solute transport parameters, such as dispersion coefficients and dispersivity were also established for the soil.

The numerical model *SandModel* was developed and used to replicate the laboratory sand tank model and to simulate field conditions at the contaminated Baruwa, Nigeria site. The model simulations predicted patterns of groundwater flow, chloride tracer flux and petroleum hydrocarbon plume advancement/dispersion in the groundwater zone. The method of finite difference was used to solve the 3-D Advection-Dispersion equation, while the FORTRAN computer language was used to code the algorithm and develop the *SandModel* computer code. The results were displayed graphically using the MATLAB application package. The Laboratory and Field-Scale *SandModel* is applicable to conservative and reactive solute transport modeling at the laboratory and field scale configuration and has been validated for porous media materials. The plots of the tracer breakthrough curves (TBCs) for the twelve (12) multi-level observation points within the model domain show a reasonable match of the simulated and observed tracer breakthrough curves. Calculated t (Paired- t -statistic (student t quantile)) value for each observation well is less than the critical value of t ($t_{critical} = 2.16$ for $df=13$), and the calculated P value for each well is greater than the chosen significance level ($P=0.05$), therefore the null (no difference) between observed and simulated data sets hypothesis is accepted. The analysis also

reveals high to very high correlation ($R^2=0.79$ to $R^2=0.91$) between the observed and simulated values. A sensitivity analysis showed that the time required for complete source depletion, was most dependent on the source definition, biodegradation rate and the hydraulic conductivity K of the porous medium.

Soil particle size (D_{50}) and hydraulic conductivity (K) data have been used to establish a correlation between the hydrodynamic transport parameters (Dispersivity [α]) for the laboratory and field porous media soils. The proposed empirical relation for the determination of the field dispersivity [α] parameter is;

$$\frac{D_{50(L)}}{D_{50(F)}} \left(\frac{K_{(L)}}{K_{(F)}} \right) = \frac{\alpha_{(F)}}{\alpha_{(L)}}$$

A Retardation factor, $R = 2.5$, and biodegradation rate of 0.0004/day (half life of 5 years) were obtained from the model calibration for BTEX. A clean-up time for BTEX of about 45 years was estimated by natural attenuation from model predictions.

The results are highly relevant in the light of the increasing awareness of the precarious trend of lack of monitoring and remedial feasibility data for the subsoil environment in the thousands of gasoline fuel stations, and petroleum storage/distribution underground infrastructure in Nigeria.

TABLE OF CONTENTS

	PAGE
Title page	i
Certification page	ii
Acknowledgements	iii
Dedication	iv
Abstract	v
Table of Contents	vii
List of Tables	xi
List of Figures	xii
List of Plates	xiv
List of Appendices	xv
Symbols and Abbreviations	xvi
 CHAPTER ONE: INTRODUCTION	 1
1.1 Background to Research Work	1
1.2 Problem Statement	3
1.3 Scientific Hypotheses	3
1.4 Justification	4
1.5 Aim and Objectives	4
1.5.1 Aim	4
1.5.2 Objectives	5
1.6 Expected Output	5
 CHAPTER TWO: LITERATURE REVIEW	 6
2.1 Description of Contaminant Source Zones	6
2.2 Environmental Fate of Organic Chemicals	7
2.3 Chemicals of Concern	7
2.4 Light Nonaqueous Phase Liquids (LNAPL)	8
2.5 Principles of Migration and Fate of Contaminants	10
2.6 Soil Contamination	10
2.6.1 Ecosystem Effect	12
2.6.2 Health Effect	12
2.7 Occurrence of Groundwater Contamination	12
2.8 Groundwater Quality	13
2.9 Regulatory Framework	14



2.10 Petroleum Production and Exploration in Nigeria	15
2.11 Petroleum Hydrocarbon	17
2.11.1 Functional Groups	18
2.12 Oil Spills in Nigeria	19
CHAPTER THREE: METHODOLOGY	22
3.1 General Overview	22
3.2 Setting-up of the Laboratory Aquifer Model	23
3.2.1 Construction of the 3-D Sand Tank Model	23
3.2.2 Soil/Groundwater Sampling, Monitoring & Testing	26
3.2.3 Contaminant Fate & Transport Modeling	27
3.3 Field Work on the Case Study Site	28
3.3.1 Site Description/Experimental Programme	28
3.3.2 Preliminary Site Reconnaissance & Desk-Top Review	29
3.3.3 Geographical Setting	30
3.3.4 Community Population & Occupation	32
3.3.5 Site Characterization, Sampling & Testing Programme	32
3.3.6 Soil Sample Collection	33
3.3.7 Water Sample Collection	33
3.3.8 Sample Handling & Preservation	33
3.3.9 Analysis of Soil Samples	34
3.3.10 Analysis of Water Samples	34
3.4 Laboratory Analyses (Organic & Inorganic)	34
3.4.1 Determination of Metal Ions in Samples (Mn & Fe Total)	34
3.4.2 Determination of Dissolved Oxygen in Water Samples	35
3.4.3 Determination of TPH in Samples by GC-FID	36
3.4.4 Determination of BTEX in Samples by GC-FID	36
3.4.5 Determination of Ammonium Nitrogen in Water Samples	37
3.4.6 Determination of Sulphide in Water Samples	38
3.4.7 Sampling Methodology/Quality Control	38
3.5 Contaminant Fate & Transport Modeling/Remedial Design (Field-Scale Studies)	39
CHAPTER FOUR: THEORETICAL BACKGROUND	40
4.1 Fundamental Principles	40
4.2 Hydrodynamic Processes	40
4.3 Sorption of Hydrocarbons	41
4.3.1 Equilibrium Sorption	42
4.3.2 Kinetic Sorption	44

4.4	Biodegradation of Hydrocarbons	45
4.4.1	Aerobic Degradation of Hydrocarbons	46
4.4.2	Anaerobic Degradation of Hydrocarbons	47
4.4.3	Methanogenesis	48
4.5	Advective-Dispersive Transport	48
4.6	Classical Theory of Dispersion in a Porous Medium	54
4.7	The Magnitude of Dispersivity	55
4.7.1	Results Based on Homogeneous 1-D Sand Columns	55
4.7.2	Results Based on Field Studies	56
4.8	Initial and Boundary Conditions	58
4.8.1	Boundary Conditions	58
 CHAPTER FIVE: RESULTS AND DISCUSSION		60
5.1	Sand Tank Model Design and Evaluation	60
5.1.1	Groundwater Movement	60
5.1.2	Sand Tank Model	61
5.1.3	Laboratory Sand Tank (Aquifer) Model Experimental Set-up	62
5.1.4	Characterization of the Porous Media and Flow Characteristics	62
5.1.4.1	Characterization of the Owena Sand	62
5.1.4.2	Tracer Experiment: Experimental Procedures	64
5.1.5	Results/Overview of Plume Behavior	66
5.1.5.1	Observation for the Multilevel Sampling Points	67
5.1.5.2	Statistical Temporal Moments of Tracer Breakthrough Curve	68
5.1.5.3	Statistical Moments of Tracer Breakthrough Curve for the second discharge rate	69
5.2	Computer Simulation of Tracer Experiments in a Physical Aquifer Model	71
5.2.1	Physical and Numerical Modeling	71
5.2.2	Model Equations and Methods	71
5.2.2.1	Governing Equations	71
5.2.2.2	Boundary and Initial Conditions	72
5.2.2.3	Modeling Techniques and Numerical Implementation	73
5.2.2.4	<i>SandModel</i> Computer Code	77
5.2.3	Model Results and Analysis	78
5.2.3.1	Concentration Breakthrough profiles	78
5.2.3.2	Spatial Plume Description	80
5.2.4	Sensitivity Analysis	83

5.3	Plume Behaviour for Petroleum Hydrocarbon in a Tropical Sand Tank	86
5.3.1	General Overview	86
5.3.2	Materials and Methods	86
5.3.2.1	Experimental Design	86
5.3.2.2	Physico-Chemical Properties (BTEX)	86
5.3.2.3	Analytical Procedures	86
5.3.3	Results and Analysis	87
5.3.4	Modeling Hydrocarbon Reactive Transport Process	99
5.3.4.1	Advective-Dispersive/Reactive Transport	99
5.3.5	Model Results and Analysis	103
5.3.6	Sensitivity Analysis	105
5.4	The Use of Sand Tank Experiments to Simulate Field Conditions...	108
5.4.1	General Overview	108
5.4.2	Laboratory and Field Model Description	108
5.4.2.1	Laboratory Aquifer Model	108
5.4.2.2	Baruwa Field Site	109
5.4.2.3	Approximate Field Solute Transport Parameter Estimation	109
5.4.2.4	Numerical Implementation	110
5.4.2.5	Boundary and Initial Conditions	112
5.4.2.6	Analytical Procedures	113
5.4.3	Results and Analysis	114
5.4.3.1	Periodic Field Sampling and Analysis (BTEX)	114
5.4.3.2	Periodic Field Sampling and Analysis (Inorganics)	118
5.4.4	Modeling and Discussion	118
5.4.4.1	Computer Simulation	118
5.4.4.2	Model Predictions	119
CHAPTER SIX:	CONCLUSIONS AND RECOMMENDATIONS	126
6.1	Conclusions	126
6.2	Recommendations	127
REFERENCES		129
APPENDICES		137

LIST OF TABLES

TABLE	PAGE
5.1 Result of Sieve Analysis of Owena Sand	137
5.2a Estimates of Owena Sand Geotechnical, Hydraulic and Geochemical Properties	63
5.2b Sand Tank Flow Characteristics	64
5.3 Nonreactive Tracer in the Experimental Injection Solution	64
5.4 Spatial & Temporal Distribution of Chloride Conductivity for the Tracer Experiment. (1 st Port)	65
5.5 Spatial & Temporal Distribution of Chloride Conductivity for the Tracer Experiment (2 nd Port)	66
5.6 Results from Statistical Moment Analysis of TBC (Outflow Port 1)	69
5.7 Results from Statistical Moment Analysis of TBC (Outflow Port 2)	70
5.8 Co-ordinates for Observation Wells in the Sand Tank Model	75
5.9 Flow system parameters used in simulating the laboratory scale tracer experiment	78
5.10 Summary of Sensitivity	84
5.11 Properties of the gasoline components	86
5.12 Spatial Distribution of Hydrocarbon concentrations for the 1 st sampling session [Day 1]	88
5.13 Spatial Distribution of Hydrocarbon concentrations for the 2 nd sampling session [Day 8]	88
5.14 Spatial Distribution of Hydrocarbon concentrations for the 3 rd sampling session [Day 15]	89
5.15 Spatial Distribution of Hydrocarbon concentrations for the 4 th sampling session [Day 36]	89
5.16 Spatial Distribution of Inorganic concentrations for the 1 st sampling session [Day 1]	97
5.17 Spatial Distribution of Inorganic concentrations for the 2 nd sampling session [Day 8]	97
5.18 Spatial Distribution of Inorganic concentrations for the 3 rd sampling session [Day 15]	98
5.19 Spatial Distribution of Inorganic concentrations for the 4 th sampling session [Day 36]	98
5.20 Input parameters for the model	103
5.21 Summary of Sensitivity	106
5.22 Input parameters for the model	113
5.23 Properties of the gasoline components	113
5.24 Groundwater BTEX Concentration in twenty-five (25) Wells at Baruwa	114
5.25 Groundwater Inorganic Analysis in twenty-five (25) Wells at Baruwa (Sept., 2006)	138
5.26 Groundwater Inorganic Analysis in twenty-five (25) Wells at Baruwa (Dec., 2006)	139
5.27 Injected BTEX concentrations for Field-Scale Model and Simulation Results	120

LIST OF FIGURES

FIGURE	PAGE
2.1 Leakage from Underground Storage tanks (Point Source Pollution)	6
2.2 Light Nonaqueous Phase Liquid (LNAPL)	8
2.3 Map of the Niger Delta showing Province outline (maximum petroleum system)	17
2.4 Hydrocarbons	18
2.5 Derivatives of hydrocarbons	18
2.6 Hydrocarbons functional groups	19
3.1 General Flow Chart of the Research Process	22
3.2 Schematic Diagram of the Sand Tank Model	24
3.3 Layout of Baruwa community showing NNPC pipeline in dotted lines	29
3.4 Map of Nigeria showing Baruwa, Lagos, Nigeria	31
3.5 Zoom-in on Lagos showing Baruwa	31
4.1 Schematic illustration of the effects of macro-dispersion and local-scale dispersion	41
4.2 Examples of different sorption isotherm models.	43
4.3 Processes contributing to mechanical dispersion	51
5.1 Combined Particle Size Distribution curve for Samples A, B, and C	62
5.2 TBC for observation wells OW_B , OW_C and OW_D (Port 1)	67
5.3 TBC for observation wells OW_B and OW_E (Port 1)	67
5.4 TBC for observation wells OW_B , OW_C and OW_D (Port 2)	67
5.5 TBC for observation wells OW_B and OW_E (Port 2)	67
5.6 Measured Tracer Breakthrough Curve for observation well (OW_{BM})[Port 1]	68
5.7 Measured Tracer Breakthrough Curve for observation well (OW_{BM})[Port 2]	70
5.8 Rectangular Finite Difference grids for the Sand Tank Model	75
5.9a Flow Chart for Main Computer Program	76
5.9b Flow chart for Subroutines	77
5.10 Observed and Simulated Chloride Tracer Conc. Profiles for the Twelve Multi-level Obs. Points.	80
5.11 XY002 (Tracer Isoconcentration Contours after 2 hours)	81
5.12 XY004 (Tracer Isoconcentration Contours after 4 hours)	81
5.13 XY006 (Tracer Isoconcentration Contours after 6 hours)	81
5.14 XY008 (Tracer Isoconcentration Contours after 8 hours)	81
5.15 XY010 (Tracer Isoconcentration Contours after 10 hours)	81
5.16 XY030 (Tracer Isoconcentration Contours after 30 hours)	82
5.17 Tracer Plume at Observation Well B; Top,Middle,Bottom, 8 hours (YZ View)	82
5.18 Tracer Plume at Observation Well B; Top, Middle, Bottom, 8 hours (XZ View)	83
5.19 Model Sensitivity to Hydraulic Conductivity (Sampling location OW_{BM})	84

5.20	Model Sensitivity to Source Concentration (Sampling location OW _{BM})	85
5.21	Measured BTEX Breakthrough Curve for observation well (OW _{BT})	90
5.22	Measured BTEX Breakthrough Curve for observation well (OW _{BM})	90
5.23	Measured BTEX Breakthrough Curve for observation well (OW _{BB})	91
5.24	Measured BTEX Breakthrough Curve for observation well (OW _{CT})	91
5.25	Measured BTEX Breakthrough Curve for observation well (OW _{CM})	92
5.26	Measured BTEX Breakthrough Curve for observation well (OW _{CB})	92
5.27	Measured BTEX Breakthrough Curve for observation well (OW _{DT})	93
5.28	Measured BTEX Breakthrough Curve for observation well (OW _{DM})	93
5.29	Measured BTEX Breakthrough Curve for observation well (OW _{DB})	94
5.30	Measured BTEX Breakthrough Curve for observation well (OW _{ET})	94
5.31	Measured BTEX Breakthrough Curve for observation well (OW _{EM})	95
5.32	Measured BTEX Breakthrough Curve for observation well (OW _{EB})	95
5.33	Measured BTEX Breakthrough Curve for Soil around (OW _{BM})	96
5.34	Measured BTEX Breakthrough Curve for Soil around (OW _{EM})	96
5.35	Measured Iron (II) concentration for observation well (OW _{BM})	98
5.36	Measured Dissolved Oxygen concentration for observation well (OW _{BM})	99
5.37	Measured and simulated BTEX Breakthrough Curve for observation well (OW _{EM})	104
5.38	Measured and simulated BTEX Breakthrough Curve for observation well (OW _{CM})	104
5.39	Measured and simulated BTEX Breakthrough Curve for observation well (OW _{DM})	105
5.40	Measured and simulated BTEX Breakthrough Curve for observation well (OW _{EM})	105
5.41	Model Sensitivity to Retardation factor (Sampling location OW _{BM})	106
5.42	Model Sensitivity to Decay constant (Sampling location OW _{BM})	107
5.43	Finite difference grid for the Field-scale model	111
5.44	BTEX Isoconcentration -mg/l [September, 2006]	115
5.45	BTEX Isoconcentration -mg/l [December, 2006]	116
5.46	Total Hydrocarbon Isoconcentration -mg/l [June, 2006]	117
5.47	Liquid Hydrocarbon Thickness above Water Surface (m) [June, 2006]	117
5.48	Direction of Ground Water Flow	118
5.49	0.5 year [6 months] of BTEX (mg/l) simulation (1994)	121
5.50	A Comparison of Simu. (contoured) and Obs. (symbols) BTEX Conc. in the x-y Plane for 12 years	122
5.51	20 years of BTEX (mg/l) simulation (2014)	123
5.52	40 years of BTEX (mg/l) simulation (2034)	124
5.53	60 years of BTEX (mg/l) simulation (2054)	125

LIST OF PLATES

PLATES	PAGE
3.1 Reinforcing Cage for Glass-Plexiglass Laboratory Sand Tank and the Elevated Water Reservoir	26
3.2 Inductively Coupled Plasma Emission Spectrometry for Metal Analysis	35
3.3 Gas Chromatography Apparatus	37
3.4 Water Purification System	38

LIST OF APPENDICES

APPENDIX	PAGE
A1	137
A2	140
B	152
C	164
D	168

SYMBOLS AND ABBREVIATIONS

SYMBOLS

- D_{50} median particle diameter [L].
- n Total porosity [-].
- n_e effective porosity [-].
- f_{oc} Organic carbon weight fraction [-].
- h Head [L].
- C_u Coefficient of uniformity [-].
- C_g Coefficient of gradation/curvature [-]
- P Peclet number, [-].
- D_e effective diffusion coefficient $L^2 T^{-1}$
- K_d distribution coefficient $L^3 M^{-1}$
- K tensor of hydraulic conductivity $L T^{-1}$
- C_w Solute concentration
- C_s Solid phase concentration
- K_F Freundlich coefficient
- $1/n_F$ Freundlich exponent
- K_L Langmuir coefficient
- q specific discharge
- S_s specific storage coefficient
- q_s source/sink term
- r radius of the idealized spherical particle
- D_a apparent diffusion coefficient.
- J_v advective mass flux
- J_m dispersive mass flux
- J_d diffusive mass flux
- M_c solute mass
- M_s sorbed mass
- s sorbed mass with respect to the pore volume
- D_m mechanical dispersion tensor

- $t_{1/2}$ half-life
 c solute mass/concentration
 $D^* = D_d \tau$ is the effective diffusion coefficient
 $D_{i,w}$ free-solution diffusion coefficient [L^2/T].
 H_d Henry's Law constant [$atm.L^3/mol$]
 K_{oc} Octanol-Water partition coefficient [L^3/M].

Greek Letters

- ν kinematic viscosity [L^2/T].
 α dispersivity
 α_l longitudinal dispersivity
 α_t transverse dispersivity
 λ decay constant
 τ tortuosity
 ρ_b porous medium bulk density

ABBREVIATIONS

- BTEX Benzene, Toluene, Ethylbenzene and Xylenes
PAH Polycyclic Aromatic Hydrocarbons
TPH Total Petroleum Hydrocarbon
MTBE Methyl tert-Butyl Ether
EA Electron Aceptor
ED Electron Donor
MNA Monitored Natural Attenuation
MT3D Modular Transport model in 3 Dimensions
RT3D Reactive Transport model in 3 Dimensions
NAPL Non-aqueous Phase Liquid
LNAPL Light Non-aqueous Phase Liquid
DNAPL Dense Non-aqueous Phase Liquid
MCL Maximum Contaminant Level
ppm part(s) per million
US EPA United States Environmental Protection Agency
DO Dissolved Oxygen
WQB-7 W.H.O Water quality standard
VOC Volatile Organic Compounds

CHAPTER ONE

INTRODUCTION

1.1 Background to the Research Work

Soil and groundwater contamination by organic chemicals such as petroleum fuels, coal tar and creosote is a serious concern at many industrial facilities and waste disposal sites. In their pure form, these chemicals are non-aqueous phase liquids (NAPL) (Mackay et al., 1991). NAPL in the form of immobile residual contamination, or pools of mobile or potentially mobile NAPL, can represent continuing sources of groundwater contamination unless NAPL zones are removed from the subsurface, isolated from the groundwater system, or treated in situ. NAPLs can flow in the subsurface. Those less dense than water (LNAPLs) are not usually found below the water table. NAPLs more dense than water (DNAPLs) can flow below the water table. Crude oil and its derivatives contain hydrocarbon components that have significant solubility in water. Essentially all chemical contaminants can dissolve in groundwater to some extent and therefore move along with flowing groundwater.

Subsurface hydrogeology of any area is typically divided into the unsaturated (soil moisture) zone and the saturated (groundwater) zone. The site geology will form the physical framework through which the groundwater and contaminants flow. Thus, the geologic model should describe the hydrogeology, and the accuracy of geologic study directly influences the subsurface drilling, sampling, mapping and the hydrogeologic study. Freeze and Cherry (1979) describe the basic groundwater transporting processes for contaminant plume solutes as advection and hydrodynamic dispersion. Advection is the process by which groundwater in motion carries dissolved solutes. Hydrodynamic dispersion comprises of molecular diffusion and the mechanical mixing components.

The goal of site remediation is to restore soil and groundwater quality to precontamination conditions. Site remediation considers the limit of technical expertise, existing government regulations, environmental protection desired and economics. Numerous technologies to remediate

sites exist, namely, Excavation, Air stripping, Carbon bed adsorption, Incineration (Thermal destruction), Bioremediation, Soil vapour venting and Natural Attenuation (Ola and Ojuri, 2008). The selection of the most appropriate soil and sediment remediation technique depends on the site characteristics, concentration/types of contaminants to be removed and the end use of the contaminated medium. The approaches include isolation, immobilization, toxicity reduction, physical separation, extraction and bioremediation.

When examining soil problems, the location, conditions and behaviour of groundwater must be given thorough consideration (Nolan et al., 2007). Hiscock et al. (1995) investigated groundwater vulnerability assessment using geographic information system (GIS) methodology for two case studies. In the first case study, a GIS was used to create a groundwater vulnerability map of the Midlands of northwest of England by overlaying regional information on the solid geology, quaternary drift cover and soil cover. The map revealed that areas of extreme and high groundwater vulnerability occur in the vicinities of Birmingham, Liverpool and Manchester. In the second study a GIS was used to create a groundwater vulnerability map for Southeast England and to combine this information with results from a routing model for the transport of hazardous aqueous waste within the region. It was concluded that a GIS methodology is very suitable for groundwater vulnerability mapping, providing an ability to integrate multiple layers of information and to derive additional information, for examples on pollution risks.

Several authors (Leland and Hillel, 1981; Torres et al., 2007; Mirbagheri and Hashemi Monfared, 2009) have also investigated the effect of the condition of groundwater on the soil properties. By examining aspects of groundwater pollution by organic chemicals it was shown that many mechanisms are not properly understood and research programmes are required. The scale of the problem was discussed by Capel et al. (2008).

During a 3-year period Lethomaki (1975) studied the possibility of influencing, the rate of oil degradation in soil by (a) improving the conditions of microbial life with aeration, irrigation and

fertilizers (b) adding microbes (bacteria and yeast). If nothing is done to accelerate the process, oil may persist in soil for many years.

In October 1989, USEPA issued a memorandum which stated that 'pump-and-treat' technology is incapable of achieving the agency's groundwater remediation objectives. The reasons cited for this limitation included; heterogeneity of contaminated regions, failure to control continued contamination from source zones, inadequate system design and fundamental limitations of the process to remove occluded and adsorbed phase material (US EPA, 1999). As the limitations of the traditional 'pump-and-treat' groundwater treatment processes have become more broadly recognized (Mackay and Cherry, 1993), scientists and engineers have sought enhancements and alternatives, which would provide more rapid and reliable remediation of contaminated aquifers.

1.2 Statement of the Problem:

The precarious trend of the lack of monitoring and remedial feasibility data for the subsoil environment in the thousands of gasoline fuel stations, and petroleum storage/distribution underground infrastructure in Baruwa community, Lagos, Nigeria and Nigeria as a whole is the problem.

1.3 Scientific Hypotheses:

1. Petroleum Hydrocarbon leaked from petroleum pipelines continue to impact the subsurface aquifer through the dissolution of entrapped pure phase hydrocarbon in the soil pores at the water table and the horizontal or inclined flow of the dissolved contaminant with groundwater. The residual hydrocarbon in soil pores act as a secondary source of dissolved contaminants in the ground water.
2. Unconsolidated lateritic soils, granular backfill and sand lenses act as preferential pathways of contaminant migration in the subsurface, especially in the unsaturated soil moisture zone, and this hastened the pace of the leaked hydrocarbon through the thick surficial aquitard in Baruwa.

3. Integration of laboratory-scale and field-scale aquifer models using numerical modeling techniques will lead to a versatile remedial feasibility design tool with both retroactive and predictive capabilities.
4. Integration of active and passive remediation techniques will lead to an optimal low-cost remediation technology for the study area.
5. Enhancement of natural processes (physical, chemical and biological) through engineered/controlled natural attenuation will produce an appropriate and sustainable remediation technique.

1.4 Justification:

The impact of crude oil exploitation activities and petroleum products pipeline distribution on human and ecological receptors in Nigeria is a major concern, with regards to human/ecological receptor's health and environmental sustainability objectives. The analysis of dissolved contaminant fate and transport from source areas containing non-aqueous phase liquids (NAPL) is an important component in the evaluation of the risk posed to down gradient receptors, of monitoring plan development, and of remedial alternative selection. This research will contribute to the effective management of land and groundwater resources in Nigeria and other developing countries. Effective management of our environmental resources would certainly contribute to the eradication of extreme poverty and hunger, and ultimately ensure environmental sustainability, thereby addressing goals number one (1) and number seven (7) of the United Nations' Millennium Development Goals (MDG) (Victor, 2008).

1.5 Aim and Objectives:

1.5.1 Aim:

This was to conduct an experimental and numerical investigation focused on characterizing the source, extent, transport and fate of petroleum hydrocarbon

contamination in a 3-D sand tank model/case study field site (Baruwa), appraising the implication of the results for evaluating remediation endpoints.

1.5.2 Objectives:

The specific objectives were to:

- i. characterize the aquifer material for the laboratory and field site;
- ii. Develop a 3-D laboratory aquifer (sand tank) model;
- iii. evaluate the use of multilevel wells and existing hand dug wells for the characterization and location of hydrocarbon residuals and the plume of dissolved hydrocarbons;
- iv. determine the transport and fate of Benzene, Toluene, Ethylbenzene, Xylene (BTEX) from petroleum hydrocarbon, within the subsurface aquifer using the laboratory model and a field site; and
- v. develop a predictive numerical model '*SandModel*' which replicates the laboratory sand tank model for the simulation of longer term transport and natural attenuation of the hydrocarbon in groundwater.

1.6 Expected Output:

The research is expected to:

- (i) provide an innovative design of a laboratory aquifer model (3-D sand tank) for subsurface contamination assessment and remediation techniques evaluation;
- (ii) enhance the determination and characterization of the extent of soil and groundwater contamination in the area of case study;
- (iii) establish the assimilative capacity of the natural processes to degrade the impacts documented at the site; and
- (iv) establish the predictive numerical model '*SandModel*' for the simulation of contaminant transport and natural attenuation in the subsurface soil/groundwater.

CHAPTER TWO

LITERATURE REVIEW

2.1 Description of Contaminants Source Zones

Sources of soil/groundwater contamination from petroleum hydrocarbon include oil spillage and leakage from pipeline and storage facilities (see Figure 2.1). These sources can be described as follows;

- Point sources: specific and determinable sites of entry that can be regulated (e.g., pipe discharge, smokestack plumes)
- Non-point sources: diffuse or multiple sites of entry that are not easily regulated (e.g., agricultural runoff, atmospheric deposition, volatilization from land)

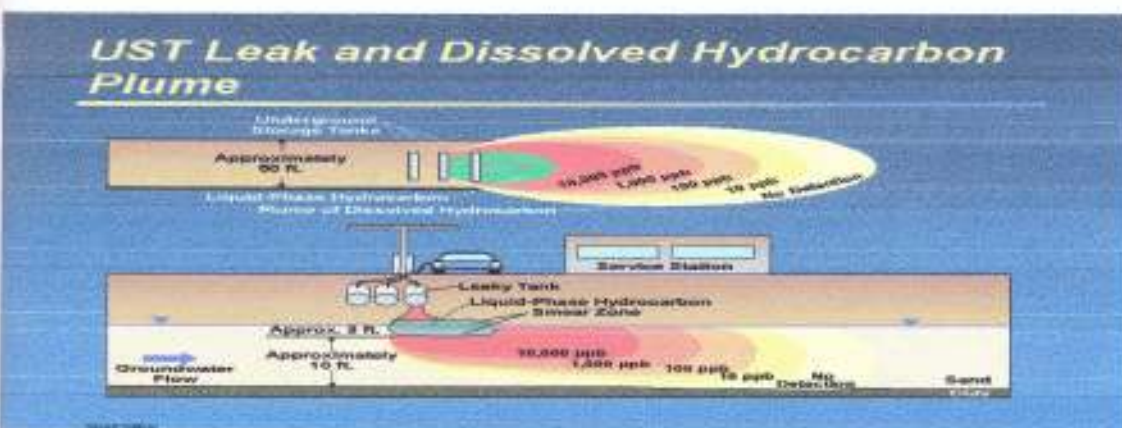


Figure 2.1: Leakage from Underground Storage tanks (Point Source Pollution) (Parsons, 2004)

Pollutants from point sources are generally related to urban development, while diffuse sources are generally rural in nature. The most significant diffuse contaminant of groundwater is nitrate, due to its adverse affects on people, animals and the environment (Rinaudo, 2003). The most significant point-source contaminants include underground storage tanks (hydrocarbons), septic tanks, and landfills. Diffuse-source pollution can occur over large areas and involve widespread land-use practices or numerous small sources.

2.2 Environmental Fate of Organic Chemicals

Environmental Organic Chemicals are organic chemicals released into the environment as a result of human activities that affect human and ecosystem health at very low concentrations (i.e., mg/l concentrations or lower); or natural (biogenic) organic substances that are useful as molecular markers of environmental processes (Gavrilescu et al., 2009). It is pertinent to understand and predict processes which govern the behavior and fate (phase transfer and reaction) of organic chemicals in the environment. The most important issues to study in environmental organic chemistry are (USEPA, 1986) :

- sources, sinks, exposure, transport and transformation. (S^2ET^2)
- physicochemical properties of organic compounds
- the holistic environmental distribution of organic chemicals using simple models

2.3 Chemicals of Concern

Priority hydrocarbon pollutants can be classified as;

> Soluble/Volatile substances

- Example BTEX (Benzene, Toluene, Ethyl Benzene and Xylene)
- MTBE (Methyl tertiary-Butyl Ether)

> Persistent, bioaccumulative, and toxic substances (PBTs)

- Example PBTs
 - PAHs (polycyclic aromatic hydrocarbons)
 - PCBs (polychlorinated biphenyls)
 - Dioxins and Furans
 - Pesticides
 - PBDEs (Polybrominated diphenyl ethers)

> Emerging Contaminants

- Pharmaceuticals (human and vet)
- Perfluorinated acids (derived from Teflon)
- Fragrances



- Detergents

➤ Biogenic Substances

- Fatty acids
- Sterols

2.4 Light Non-aqueous Phase Liquids

LNAPL is a convenient label for petroleum liquids in soils and groundwater. The acronym stands for Light Non-aqueous Phase Liquid. "Light" highlights the fact that petroleum liquids are (with a few minor exceptions) less dense than water. "Non-aqueous" highlights the fact that petroleum liquids do not mix with water. (see Figure 2.2)

In more detail, LNAPLs are derived from crude oil. Common LNAPLs include fuels, lubricants, and chemical feed stock for manufacturing.

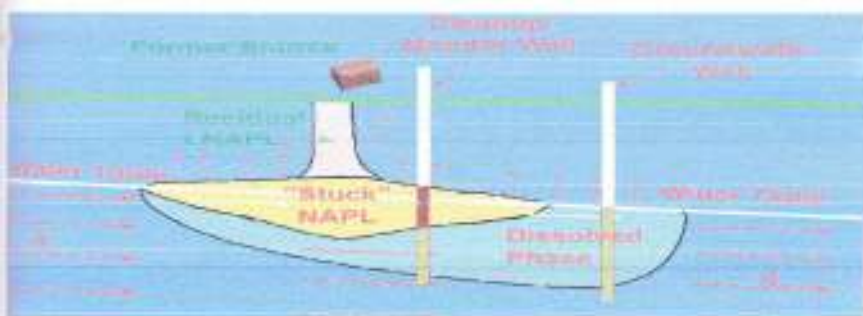


Figure 2.2: Light Non-aqueous Phase Liquid (LNAPL) (Bear, 2000)

From an environmental perspective, key features of LNAPL include:

- 1) LNAPLs are typically found at the top of groundwater zones. The buoyancy of LNAPL in water inhibits LNAPL migration into the groundwater zone.
- 2) When combined, LNAPL and water are immiscible. The net result is that subsurface LNAPL and water share pore space in soils and rock impacted by LNAPL. This "sharing of pore space" limits the mobility of LNAPL and complicates its recovery. Recognizing LNAPL releases as a problem involving multiple fluid phases in pore space is essential to developing effective solutions for LNAPL releases.

3) LNAPLs are composed of mixtures of organic molecules that are slightly soluble in water.

Where LNAPL comes in contact with groundwater, trace to low percent concentrations of the organic compounds dissolve into it. This often results in exceedances of water quality standards close to releases. A benefit of low solubility is that loading to the environment is typically small and natural processes often attenuate contaminants of concern over small distances. A disadvantage of low solubility is that LNAPL can persist as a source of groundwater contamination for extended periods.

At contaminated field sites, depending on the history of the spill and the heterogeneity of the subsurface, the trapped NAPLs (non-aqueous phase liquids) remain either in the form of blobs or as small pools. Dissolution of contaminants from trapped NAPL blobs and/or NAPL pools is a critical process that would control the overall quality of the contaminated subsurface soil and associated ground water (Chrysikopoulos and Lee, 1998; Lee and Chrysikopoulos, 1998; Clement et al., 2004). However, most of the laboratory experiments completed so far employ small-scale, one- or two-dimensional soil columns. Only a limited number of experimental studies have focused on characterizing NAPL dissolution process under three-dimensional flow conditions. NAPLs are generally of sufficiently low aqueous solubility and volatility that their limited dissolution into ground waters or volatilization into gases has resulted in predictions of their residence in the subsurface for tens, hundreds or perhaps thousands of years. However, their toxicity is often such that their solubilities are many times the permitted maximum contaminant levels allowed by the U.S. Environmental Protection Agency in drinking water. For example, the most common NAPL contaminant found in ground waters beneath gasoline stations, the component benzene, has an aqueous solubility of 1780 milligrams/liter but a maximum contaminant level of 5 micrograms/liter. Partly because of their ubiquitous use in industry and commerce, low maximum contaminant levels and mobility in the subsurface in dissolved and gaseous states, NAPLs and NAPL constituents, such as benzene derived from gasoline, have come to occupy a central place in the technical and regulatory processes associated with the characterization and remediation of hazardous waste sites.

In addition, NAPLs have become the focus of this concern because of the extreme difficulty in detecting their presence. In the context of this discussion, "detection" means the act of inferring the amount, location and/or composition of the NAPL. (MacKay and Cherry, 1993)

2.5 Principles of Migration and Fate of Contaminants

The most important processes in the transport of solutes in groundwater (Freeze and Cherry, 1979, Domenico and Schwartz, 1990,) are:

- Advection: the processes whereby the solute is carried by the average groundwater velocity through the porous medium;
- Mechanical dispersion: the processes that cause variations from the average transport pathway on account of the tortuous structure of the pore space of natural porous media;
- Diffusion: the net result of the average molecular motion of the solute molecules in the pore water;
- Sorption: the process whereby solute molecules attach themselves to surfaces of soil grains;
- Decay: radioactive or biological processes that transform the solute into other substances.

2.6 Soil Contamination

Soil contamination is the presence of man-made chemicals or other alteration of the natural soil environment. This type of contamination typically arises from the rupture of underground storage tanks, leakage of petroleum pipes, application of pesticides, percolation of contaminated surface water to subsurface strata or direct discharge of industrial wastes to the soil. The chemicals mostly involved are petroleum hydrocarbon, lead and other heavy metals. This occurrence of petroleum is correlated with the degree of industrialization and intensity of chemical usage.

The extent of contaminated land is mostly well known, in North America and Western Europe, with many countries in these areas having legal frame works to identify and deal with this

environmental problem. Developing countries are the next generation of new soil and groundwater contamination cases (Rath et al., 2009).

In China, the state Environmental Protection Administration believes it to be a threat to the environment, food safety and sustainable agriculture. According to a scientific sampling, 100,000 square kilometers of Chinese cultivated land have been polluted with contaminated water being used to irrigate a further 21,670 square kilometers and another 1,300 square kilometers covered or destroyed by solid waste. In total, the area account's for one-tenth of China's cultivated land and is mostly in economically developed area. An estimated 12 million tonnes of grain are contaminated by heavy metals every year causing direct losses of US\$2.57 billion (Dong et al., 2009).

The United States, while having some of the most wide spread oil contamination, has actually been a leader in defining and implementing standards for clean up. Other industrialized countries have a large number of contaminated sites, but lag behind the US in executing remediation (Capel et al., 2009).

The ecological effect of petroleum hydrocarbon contaminated soil has been the subject of several investigation and extensive reviews (Salanitro et al., 1997 and Rinuado 2003). Many variables influence the biological effect of petroleum products on the environment. These include type and volume of petroleum product, time of year, type of receiving environment, degree of dispersion or spread weather conditions, type of clean up and rate of weathering among others (Wang et al., 2009).

Soil contaminated with crude oil has been observed to show large increases in organic matter, total carbon and nitrogen compared with normal soils. These changes were attributed to the activity of microorganisms converting hydrocarbon to atmospheric nitrogen and other organic materials (Kolehmainen et al 2009). These soils consequently exhibit deflocculating and loss of structure and are therefore more subject to erosion. Moreover, this type of soil does not support plant growth.

The effects of soil contamination are as follows;

2.6.1 Ecosystem effect

Without mincing words, soil contamination is very dangerous to an ecosystem. There are radical soil chemistry changes, which can arise from the presence of many hazardous chemicals even at low concentration of the contaminants. These changes can manifest in the alteration of metabolism of endemic microorganism and arthropods residing in a given soil environment (Li et al., 2009). This may lead to reduction of primary food chain, which in turn has major effect on predators or consumer species.

2.6.2 Health effect

There are many areas where people are in direct contact with soil. These are residential areas, schools, playing grounds, farm etc. contamination of drinking water or inhalation of soil contaminant which have vaporized, is another contact mechanism. There is a very large set of health consequences from exposure to soil contamination depending on pollutant type, pathway of attack and vulnerability of the exposed population. Petroleum hydrocarbon and many of the pesticide and herbicide formulations are carcinogenic to all human population. Another contaminant hazardous to young children is lead.

2.7 Occurrence of Ground Water Contamination

Groundwater contamination occurs when ground water in the zone of saturation is recharged with contaminated water or other liquid contaminants, or when a contaminant is placed or buried in the saturated zone. For instance, groundwater contamination may result from rain water passing through sediment contaminated with industrial or agricultural chemicals. Water polluted while on the surface of the ground, such as runoff contaminated with de-icing chemicals applied to roads in the winter, can also percolate into ground water and pollute it. Contamination may also result from wells, improperly sealed or abandoned, that allow contaminated surface water to reach an aquifer. These same wells may also transmit water from one aquifer to another if the well is drilled through

more than one aquifer. Where two aquifers are connected without the presence of a well, some natural contamination may result from direct contribution of water from an aquifer with naturally poor quality water to an aquifer having water of naturally good quality.

2.8 Ground Water Quality

Groundwater quality impacts resulting from leaking underground petroleum storage tanks are of significant environmental concern due to the sheer number of such underground tanks and the extent of possible environmental contamination when they leak. Many of these tanks are being removed and replaced or upgraded to eliminate the source of possible petroleum contamination to underlying aquifers. However, there remains a large number of sites with groundwater contamination above existing water quality limits (300,000 confirmed releases as of June 1995, with an additional 100,000 releases expected by 2000 [U.S.EPA1995]). While contamination from petroleum storage tank releases can have a significant impact on public health and the environment, active remediation of these contaminated sites can be difficult and expensive. Expectations of having to apply active remediation at all sites has generally not allowed the focusing of resources on those sites representing the greatest threat to public health and the environment (Steele et al., 2008).

When gasoline is released into the sub-surface, it distributes among the soil, gas, and aqueous phases that make up this environment. As it moves through the unsaturated zone, it leaves behind vapors containing volatile gasoline components and residual liquid hydrocarbons retained within the soil matrix. A small fraction of gasoline is water soluble and migrates to underlying aquifer with infiltrating water. Plumes of ground water hydrocarbon contamination spread within the soil environment by ground-water advection and diffusion. Many gasoline components are biodegradable, and a primary mechanism for their transformation in the subsurface is via biodegradation (Hancock et al., 2008).

The goal of site remediation is to restore soil and groundwater quality to precontamination conditions. Site remediation considers the limit of technical expertise, existing government regulations, environmental protection desired and economics. Numerous technologies to remediate sites exist, namely, excavation, air stripping, carbon bed adsorption, incineration (thermal destruction), bioremediation, soil vapour venting and natural attenuation (Ola and Ojuri, 2008). The selection of the most appropriate soil and sediment remediation technique depends on the site characteristics, concentration/types of contaminants to be removed and the end use of the contaminated medium. The approaches include isolation, immobilization, toxicity reduction, physical separation, extraction and bioremediation.

Petroleum hydrocarbons such as gasoline are extensively used in various transportation and industrial operations. Improper disposal and/or accidental release of these chemicals have resulted in several large scale ground water contamination problems (Clement et al., 2000; Clement et al., 2002). Since 1990's, it has become apparent that many fuel stations and industrial sites in Nigeria are receiving organic liquids, such as petroleum hydrocarbons and chlorinated solvents, which subsequently migrate into the subsurface beneath these sites. Once in the subsurface, these liquids dissolve and cause the contamination of groundwater supplies and then prove resistant to their quantitative removal by the remedial approaches available.

2.9 Regulatory Framework

Until about 1970's, there was little wide spread awareness of the world wide scope of soil contamination or health risks. In the United States, passage of the National Environmental Policy Act in 1969 required careful analysis of the consequence of many Federal funded projects. Passage of the Resources Conservation and Regulatory Act (RCRA) by U.S congress in 1976 established guidelines not only for handling hazardous materials but transport and hauling, (USEPA, 1986), such as required in clean up of soil contaminants.

Moreover, preparation of a phase 1 Environment Site Assessment (ESA) has become standard practice for many parts of the Western world and Japan (CCME 1994). Less developed countries are not without a share of the menace of soil contamination. Even though the use of chemical is far less than industrialized countries, often their controls and regulatory framework is quite weak.

China, an economy that regulates double-digit annual economic growth has little or no legislation to protect the environment. Currently, given the amount of land under review, up to one-tenth of china's population cultivable land may be polluted. The degree of pollution in specific location is unclear, making both prevention and remedy difficult (Dong et al 2009).

2.10 Petroleum Production and Exploration in Nigeria

As of 2000, oil and gas exports accounted for more than 98% of export earnings and about 83% of Federal government revenue, as well as generating more than 40% of Nigeria's GDP. It also provides 95% of foreign exchange earnings, and about 65% of government budgetary revenues.

Nigeria's proven oil reserves are estimated by the US EIA (United States Energy Information Administration) at between 16 and 22 billion barrels, but other sources claim there could be as much as 35.3 billion barrels. These reserves make Nigeria the tenth most petroleum-rich nation, and by far the most affluent in Africa. In mid-2001 its crude oil production was averaging around 2.2 million barrels (350,000 m³) per day ([http:// wikipedia.org](http://wikipedia.org) 2009).

Nearly all of the country's primary reserves are concentrated in and around the delta of the Niger River, but off-shore rigs are also prominent in the well-endowed coastal region. Nigeria is one of the few major oil-producing nations still capable of increasing its oil output and unlike most of the other OPEC countries; Nigeria is not projected to exceed peak production until at least 2009. The reason for Nigeria's relative oil production level is primarily OPEC regulations on production in order to regulate prices on the international market. More recently, production has been forced to

a halt intermittently by the demands and actions of the Niger Delta's inhabitants who feel they are being exploited.

Nigeria has a total of 159 oil fields and 1481 wells in operation according to the Ministry of Petroleum Resources (see Figure 2.3). The most productive region of the nation is the coastal Niger Delta Basin in the Niger Delta or "South-south" region which encompasses 78 of the 159 oil fields. Most of Nigeria's oil fields are small and scattered, and as of 1990, these small fields accounted for 62.1% of all Nigerian production. This contrasts with the sixteen largest fields which produced 37.9% of Nigeria's petroleum at that time. As a result of the numerous small fields, an extensive and well-developed pipeline network has been engineered to transport the crude.

Much of Nigeria's petroleum is classified as "light" or "sweet", meaning the oil is largely free of sulphur. Nigeria is the largest producer of sweet oil in OPEC. This sweet oil is similar in constitution to petroleum extracted from North Sea. This crude oil is known as "Bonny light". Names of other Nigerian crudes, all of which are named according to export terminal, are Qua Ibo, Escravos blend, Brass river, Forcados, and Pennington Anfan. In terms of exportation, the U.S. remains Nigeria's largest customer for crude oil, accounting for 40% of the country's total oil exports; Nigeria provides about 10% of overall U.S. oil imports and ranks as the fifth-largest source for U.S. imported oil.

There are six petroleum exportation terminals in the country; Shell owns two, while Mobil, Chevron, Texaco, and Agip own one each. Shell also owns the Forcados Terminal, which is capable of storing 13 million barrels of crude oil in conjunction with the nearby Bonny Terminal. Mobil operates primarily out of the Qua Ibo Terminal in Akwa Ibom State, while Chevron owns the Escravos Terminal located in Delta State and has a storage capacity of 3.6 million barrels. Agip operates the Brass Terminal in Brass, a town 113 km southwest of Port Harcourt and has a storage capacity of 3,558 barrels. Texaco operates the Pennington Terminal ([http:// wikipedia.org](http://wikipedia.org) 2009).

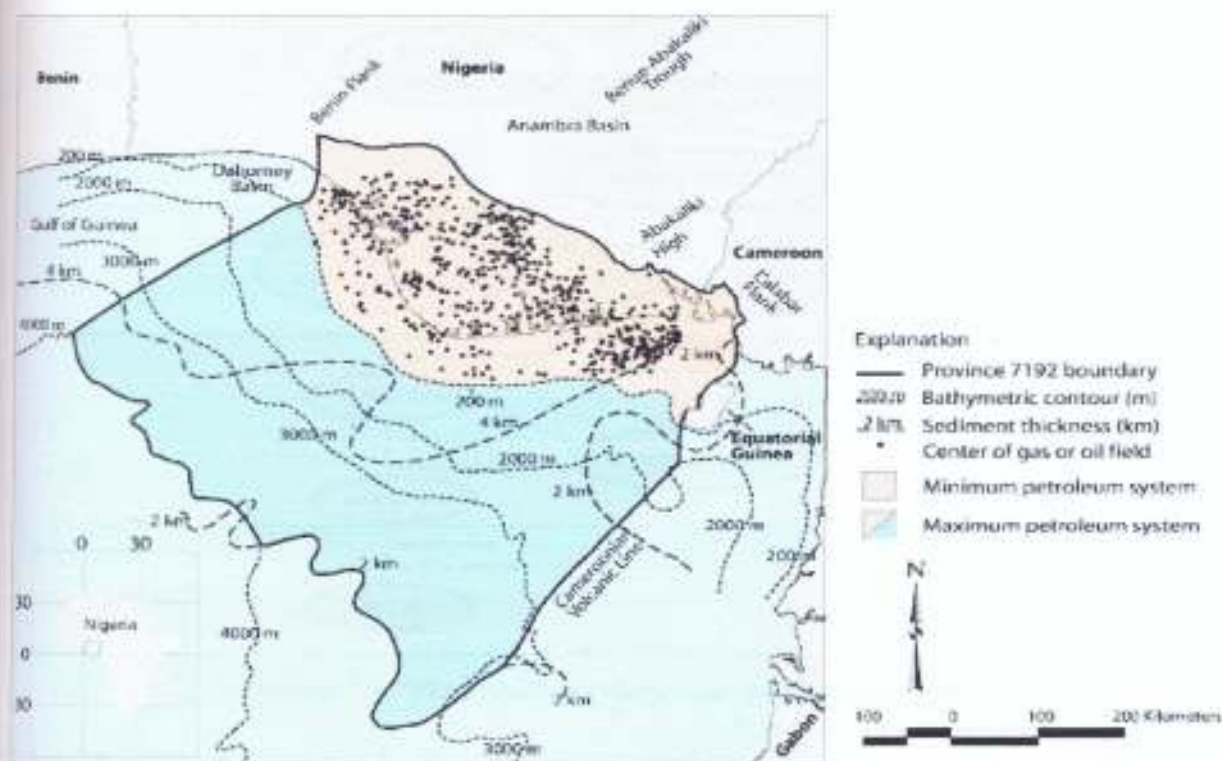


Figure 2.3: Map of the Niger Delta showing Province outline (maximum petroleum system); bounding structural features; minimum petroleum system as defined by oil and gas field center points (Petroconsultants, 1996)

2.11 Petroleum Hydrocarbon

Petroleum is a mixture of liquids varying in color from nearly colorless to jet black, in viscosity form thinner than water to thicker than molasses, and in density from light gases to asphalts heavier than water. It can be separated by distillation into fractions that range from light color, low density, and low viscosity to the opposite extreme. In places where it has oozed from the ground, its volatile fractions have vaporized, leaving the dense, black parts of the oil as a pool of tar or asphalt.

Petroleum consists mostly of hydrocarbon molecules. The four main classes of hydrocarbon are paraffin also know as Alkane, olefins also alkene, cycloparaffins also alkynes and aromatics (see Figure 2.4). The simplest hydrocarbon is one carbon atom bonded to four hydrogen atoms. It is called methane with chemical formular CH_4 (<http://gsu.edu/organic.html> 2009).

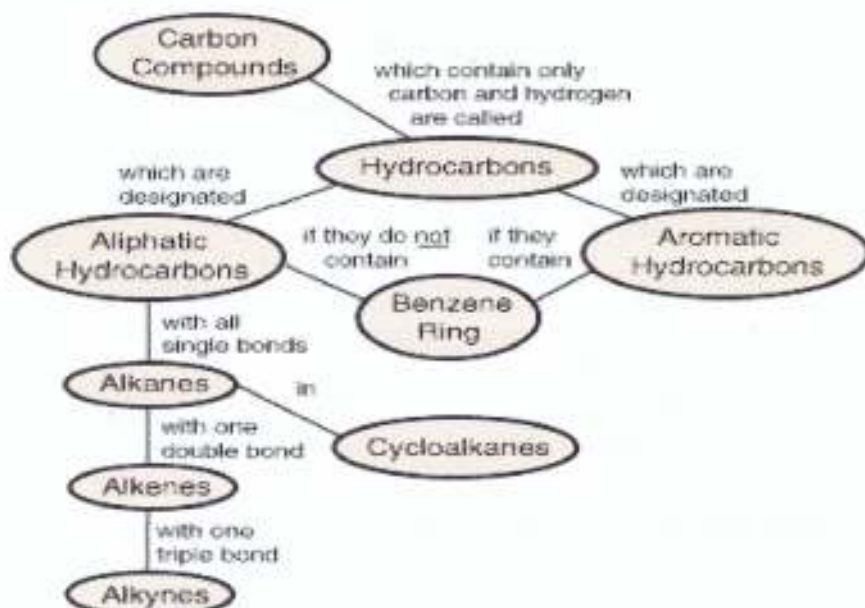


Figure 2.4: Hydrocarbons (<http://gsu.edu/organic.html> 2009)

Hydrocarbons are the simplest organic compounds. Containing only carbon and hydrogen, they can be straight-chain, branched chain, or cyclic molecules. Carbon tends to form four bonds in a tetrahedral geometry. Hydrocarbon derivatives are formed when there is a substitution of a functional group at one or more of these positions (see Figure 2.5).

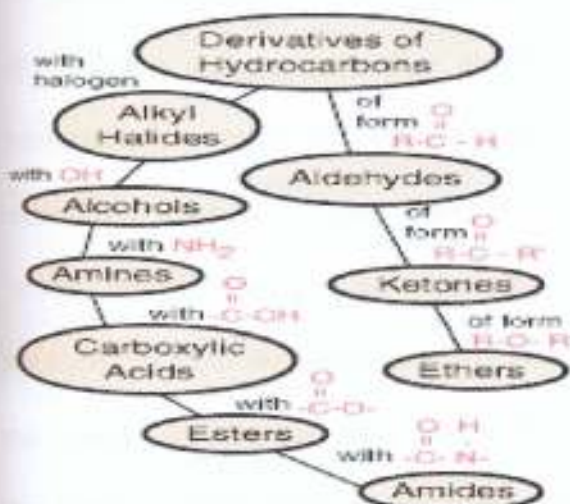


Figure 2.5: Derivatives of hydrocarbons (<http://gsu.edu/organic.html> 2009)

2.11.1 Functional groups

A functional group is a reactive portion of a molecule; particular types of reactions are associated with the functional groups described in Figure 2.6.

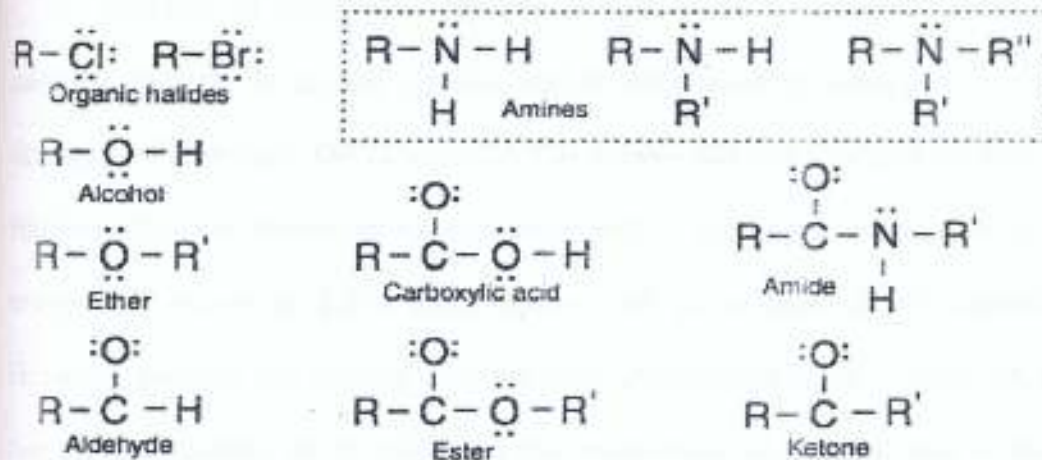


Figure 2.6: Hydrocarbons functional groups. (<http://gsu.edu/organic.html> 2009)

2.12 Oil Spills in Nigeria

Oil spills in Nigeria occur due to a number of causes which include: corrosion of pipelines and tankers (accounts for 50% of all spills), sabotage (28%), and oil production operations (21%, with 1% of the spills being accounted for by inadequate or non-functional production equipment. The largest contributor to the oil spill total, corrosion of pipes and tanks, is the rupturing or leaking of production infrastructures that are described as, "very old and lack regular inspection and maintenance". A reason that corrosion accounts for such a high percentage of all spills is that as a result of the small size of the oilfields in the Niger Delta, there is an extensive network of pipelines between the fields, as well as numerous small networks of flowlines—the narrow diameter pipes that carry oil from wellheads to flowstations—allowing many opportunities for leaks. In onshore areas, most pipelines and flowlines are laid above ground. Pipelines, which have an estimated life span of about fifteen years, are old and susceptible to corrosion. Many of the pipelines are as old as twenty to twenty-five years. Even Shell admits that "most of the facilities were constructed between the 1960s and early 1980s to the then prevailing standards. Shell Petroleum and Development Company (SPDC) would not build them that way today. Shell operates the Bonny Terminal in Rivers State, which has reportedly been in operation for forty years without a maintenance overhaul; its original lifespan was supposed to be twenty five years (Ebisemiju, 1985).

Sabotage is performed primarily through what is known as "bunkering", whereby the saboteur attempts to tap the pipeline, and in the process of extraction sometimes the pipeline is damaged or destroyed. Oil extracted in this manner can often be sold for cash compensation. The Nigerian National Petroleum Corporation (NNPC) places the quantity of oil jettisoned into the environment yearly at 2,500 cubic meters with an average of 300 individual spills annually. However, because this amount does not take into account "minor" spills, the World Bank argues that the true quantity of oil spilled into the environment could be as much as ten times the officially claimed amount. Among the largest individual spills include the blowout of a Texaco offshore station which in 1980 dumped an estimated 400,000 barrels of crude into the Gulf of Guinea and Shell's Forcados Terminal tank failure which produced a spillage estimated at 580,000 barrels. One source projects that the total amount of oil in barrels spilled between 1960 and 1997 is upwards of 100 million barrels ([http:// wikipedia.org](http://wikipedia.org) 2009).

Oil spillage has a major impact on the ecosystem into which it is released. Immense tracts of the mangrove forests, which are especially susceptible to oil (this is mainly because it is stored in the soil and re-released annually with inundation), have been destroyed. An estimated 5-10% of Nigerian mangrove ecosystems have been wiped out either by settlement or oil. The rainforest which previously occupied some 7,400 km² of land has disappeared as well.

Spills in populated areas often spread out over a wide area, taking out crops and aquacultures through contamination of the groundwater and soils. The consumption of dissolved oxygen by bacteria feeding on the spilled hydrocarbons also contributes to the death of fishes. In agricultural communities, often a year's supply of food can be destroyed by only a minor leak, debilitating the farmers and their families who depend on the land for their livelihood. Drinking water is also frequently contaminated, and sheen of oil is visible in many localized bodies of water. If the drinking water is contaminated, even if no immediate health effects are apparent, the

numerous hydrocarbons and chemicals present in oil are highly carcinogenic. Although, people often do manifest sickness following consumption of polluted water.

Offshore spills, which are usually much greater in scale, contaminate coastal environments and cause a decline in local fishing production. The decline in ecologic sustainability parallels the increase in oil production since operations began four decades ago. Furthermore, operating companies such as Shell have made public proposals for increasing production significantly in the near future which, because of the careless nature of oil operations in the Delta, will cause the environmental pollution to grow increasingly.

3.1 General Overview

The flow chart for the research project is presented in Figure 3.1. The research entails physical laboratory aquifer modeling, field studies and development of a numerical solute transport model, for the simulation of the laboratory and field experiments. Three-dimensional (3D) sand tank (1.8m x 0.3m x 0.8m) experiments were conducted to study contaminant transport and natural attenuation within the sand tank. The model was used to study the transport of an inorganic tracer (Chloride) and petroleum hydrocarbon in groundwater, within a tropical aquifer (porous media) material.

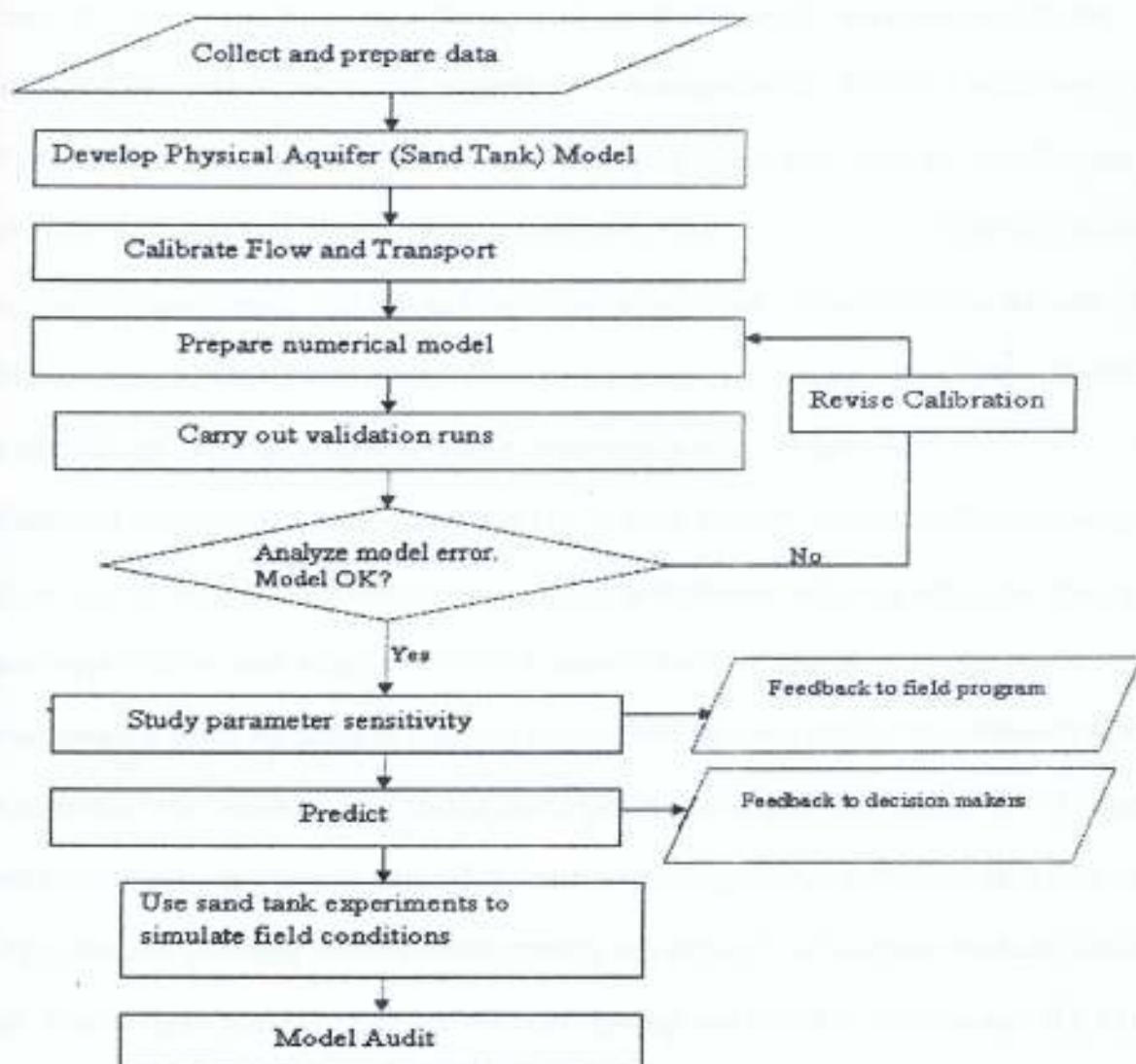


Figure 3.1 General Flow Chart of the Research Process

3.2 Setting-up the Laboratory Aquifer Model (3-D Sand Tank Model) – STAGE I

3.2.1 Construction of the 3-D sand tank model and experimental set-up

Contaminant transport and natural attenuation experiments were conducted in a three dimensional intermediate – scale glass/perspex sand tank. The sand tank was made of 1 cm thick perspex plates with dimensions of 180 cm long by 30 cm wide by 80 cm high. The perspex tank was placed in angle iron metal frame. Perforated plates located 20 cm away from both ends divide the tank into three chambers (Figure 3.2). The middle chamber was filled with a saturated alluvial porous medium (Owena sand), and the chambers at both ends with water to maintain constant heads. Variable level overflow outlets were incorporated in the constant head reservoirs, to facilitate varying of the hydraulic gradient across the porous media chamber. The experimental aquifer is 140 cm long, 30 cm wide and 80 cm high. Background data for the aquifer material including the physico-chemical and microbiological properties was first established. Sampling wells consisted of 12.5 mm diameter nested pipes, which served as multilevel observation wells for the collection of depth discrete groundwater samples. Also, the sampling pipes, which are five (5) nests of multilevel pipes, were also positioned, with first and the fifth one positioned 30 cm away from the inlet and outlet perforated separator respectively. While the central three (3) nests were arranged 70 cm away from the inlet and outlet perforated separators transversely across (Figure 3.2).

Each multilevel nest was made up of three (3) 12.5 mm diameter pipe cuts of the following length 42 cm, 62 cm and 82 cm with a plastic stopper at the lower end and a screen cut close to the plastic stopper with a mesh wrapped round it to prevent fine sand migrating into the twelve (12) number sampling ports. An adhesive tape was used to bind the three (3) 12.5 mm diameter pipes together to form the multilevel nest. On the discharge side of the sand tank model, five 18.75 mm diameter openings were drilled to create differential hydraulic gradient; with equal head difference of 0.05 m for four openings. While the fifth opening was drilled 0.025 m above the base (This is for draining the tank). One (1) 18.75 mm diameter opening was drilled on the inlet side at 0.73 m height of the sand tank model (Figure 3.2).

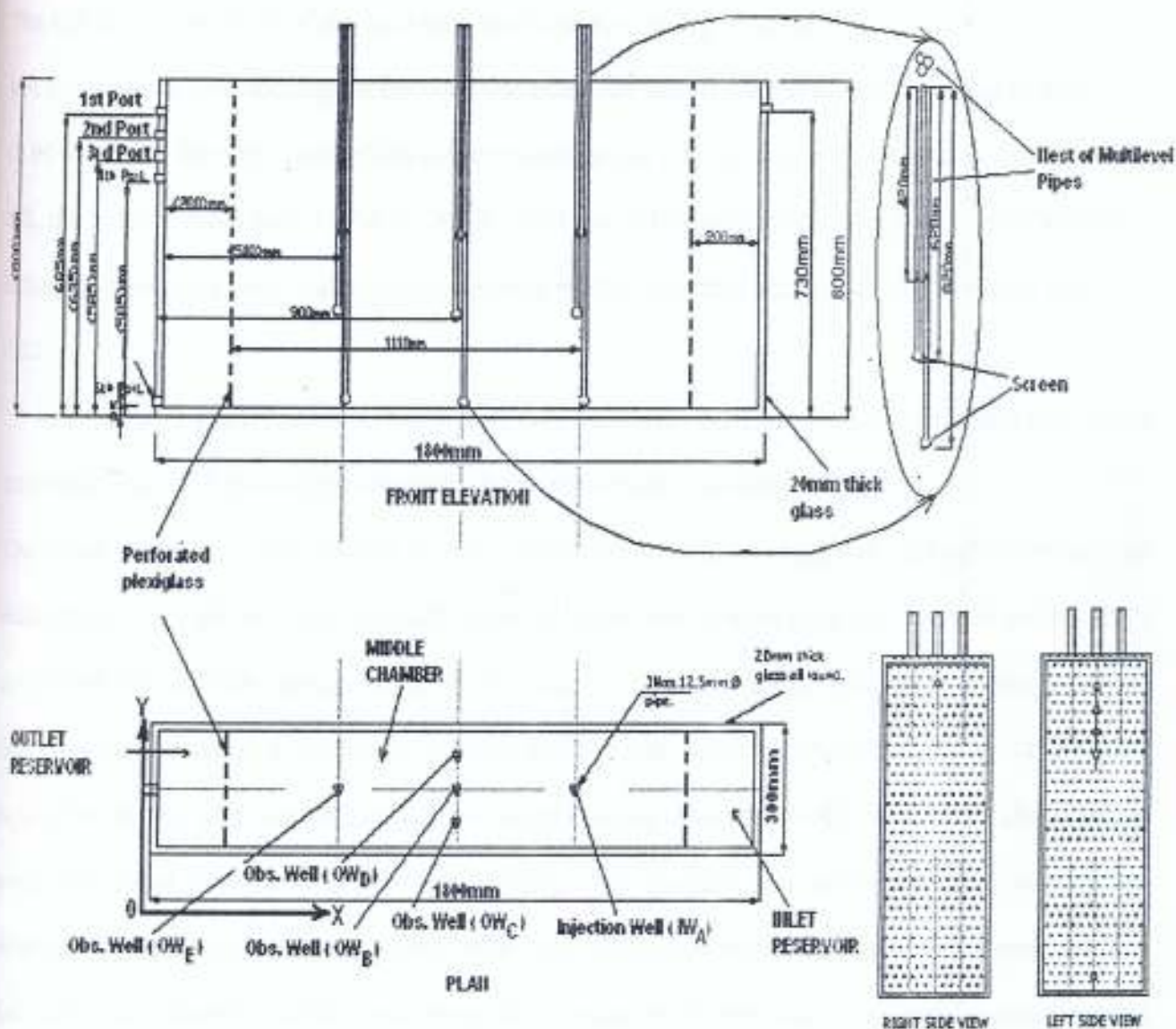


Figure 3.2: Schematic Diagram of the Sand Tank Model

In order to counter the stresses that will arise as a result of the retained material in the sand tank model, angle iron sizes of the following dimensions: 0.05 m x 0.05 m x 0.003 m thick and 0.025 m x 0.025 m x 0.003 m thick respectively were utilized to fabricate a reinforcing framework externally around the glass-perspex composite material tank. It served a dual purpose of also helping to elevate the sand tank model to position for easy monitoring; that is 0.9 m above the ground, (Plate 3.1).

A 2250 litres plastic water container was used as a source of water to the sand tank model. Water was harvested into the 2250 litres storage from the elevated roof storage tank by means of a tee connected to the discharge pipe, from the roof tank into the storage water source.

The effective invert level of the sand tank model when it is dry, without water, is 0.95 m and when it is full with the side opening on the inlet side open, the effective level of water is equal to 1.68 m, (0.95+0.73) m. The inlet level of the source water tank is 1.80 m. When the source water tank is full, the level of water in it will be 2.7 m. So, the head difference between the source water when it is full and the inlet source water in the sand tank model when it is also full at 1.68 m marks was 1.02 m.

An elevated steel, 0.75 m x 0.075 m x 0.005 m thick, platform with battered legs and braced internally, was used to hold the elevated source water tank in position (Plate 3.1).

The river sand was wet packed in the middle chamber's to minimize consolidation and air entrapment. This process was gradually done, to allow the stresses resulting from the impact to be minimized. The middle chamber's was finally filled to the brim with the river sand in lifts. The sand tank was packed under a 5cm water column, and the wet sand was compacted, to avoid grain size separation as the sand settled through the water column. The water level was raised after packing every 5cm. After sand packing the middle chambers of the sand tank model with the characterized river sand material (Owena river sand), water was allowed to flow freely through the sand medium from the inlet chamber, which was being feed continuously from the temporary storage elevated tank.

The preferred discharge port was opened, while keeping the other three (3) ports closely locked.

Water was allowed to flow freely through it for about one (1) hour, to attain a steady flow.

Thereafter, the flow rate was measured. This process was repeated for all the other three (3) ports and readings of flow rates recorded.



Plate 3.1: Reinforcing Cage for Glass-Perspex Laboratory Sand Tank and the Elevated Water Reservoir.

3.2.2 Soil/groundwater sampling, monitoring and testing

Depth discrete soil samples were also collected close to the groundwater sampling locations. A tracer transport experiment was performed to estimate the dispersivity and effective porosity values of the sand tank. Sodium Chloride was used as the chloride source. A total of 360 samples were collected during twenty four (24) sampling sessions, for the three days of the tracer experiments in the sand tank. The conductivity of the chloride tracer at the observation wells were measured using a portable Horiba U-10 Water Quality Checker (MFG. NO. 404013). The Horiba Water Quality Checker is a multimeter that is able to perform simultaneous measurement of six parameters; turbidity, electrolytic conductivity, salinity, dissolved oxygen, pH and temperature with the aid of direct-submersion sensors. The results are digitally displayed on the multimeter screen. This apparatus is available in the Water Resources and Environmental Engineering Laboratory, in the Department of Civil Engineering, Federal University of Technology Akure. The measurement

interval varied between 1 and 10 hours. A 20 ml syringe and 5 mm diameter Teflon siphon tube was used for collection of the samples into 50 ml plastic bottles. The tester, syringe and the siphon tube were rinsed with distilled water before and after each measurement.

Gasoline (petrol) was injected, at the injection well to serve as the source of contamination of the laboratory aquifer model. Four depth discrete sampling events for the soil and groundwater were conducted for four sampling locations within the aquifer model. An interval of one week was adopted for the sampling events. The parameters analysed for the soil and groundwater include; Benzene, Toluene, Ethylbenzene, and Xylene, light-end components of petroleum hydrocarbons, and are of most concern from an environmental impact perspective; dissolved oxygen (DO), an electron acceptor; carbon dioxide, a bi-product of biological activities; nitrate, an electron acceptor; Sulphate, an electron acceptor; iron (II) , a bi-product of biological activity.

3.2.3 Contaminant fate and transport modeling

The developed *SandModel* code, is a groundwater flow and solute transport simulation package developed in the Department of Civil Engineering, Federal University of Technology, Akure. This computer software was used to simulate the transport and fate of injected conservative tracer (chloride) and non-conservative LNAPL (gasoline) for the sand tank model. Input of the data generated from the groundwater sampling and identification of the hydrogeological regime were used to generate a model of the flow and contaminant transport conditions. *SandModel*, was also used to predict potential impacts down-gradient and long-term monitoring was used to validate model predictions with experimental observations. The *SandModel* contaminant transport model was used to predict the concentration and geometry of the BTEX groundwater plume. The simulation results were graphically displayed using the MATLAB application package.

3.3 Field Work on the Case Study Site: Sampling, Monitoring and Testing – STAGE II

3.3.1 Site Description/Experimental Programme

The case study site is Baruwa Community in Alimosho Local Government Area of Lagos State (Latitude 6° 35' N, Longitude 3° 16' E). This community suffered from the ruptured pipelines of Nigerian National Petroleum Corporation (NNPC)/ Pipeline Product Marketing Company (PPMC) between 1994 and 1996. The leakage went unchecked for several weeks and contaminated the underground water bodies of these areas, polluting wells and boreholes, thus rendering the waters unhealthy for consumption. Baruwa is a Community of about 90,000 people. The site area is 740 m x 900 m (Figure 3.3), consisting of over two hundred hand dug wells. Nigerian National Petroleum Corporation (NNPC) had leaking pipes running through the community from the Mosimi depot in Shagamu, Ogun State, to the Ejigbo depot in Lagos, and thus polluted the subsurface environment. The Community's hand dug wells, which has been a major source of water is now polluted. Wells and boreholes were covered by leaking products from the pipes. Tested well waters had been found to be as much as 95 percent petrol. Baruwa Village is just a few kilometres away from the state capital, Ikeja, yet the authorities have failed to stop the pipeline leakage in the community. Because of the oil leaks, hand dug wells in the community have to be kept under lock and key to prevent potential fire disasters. Clean safe water is as valuable as gold due to pollution caused by the pipelines running across the village.

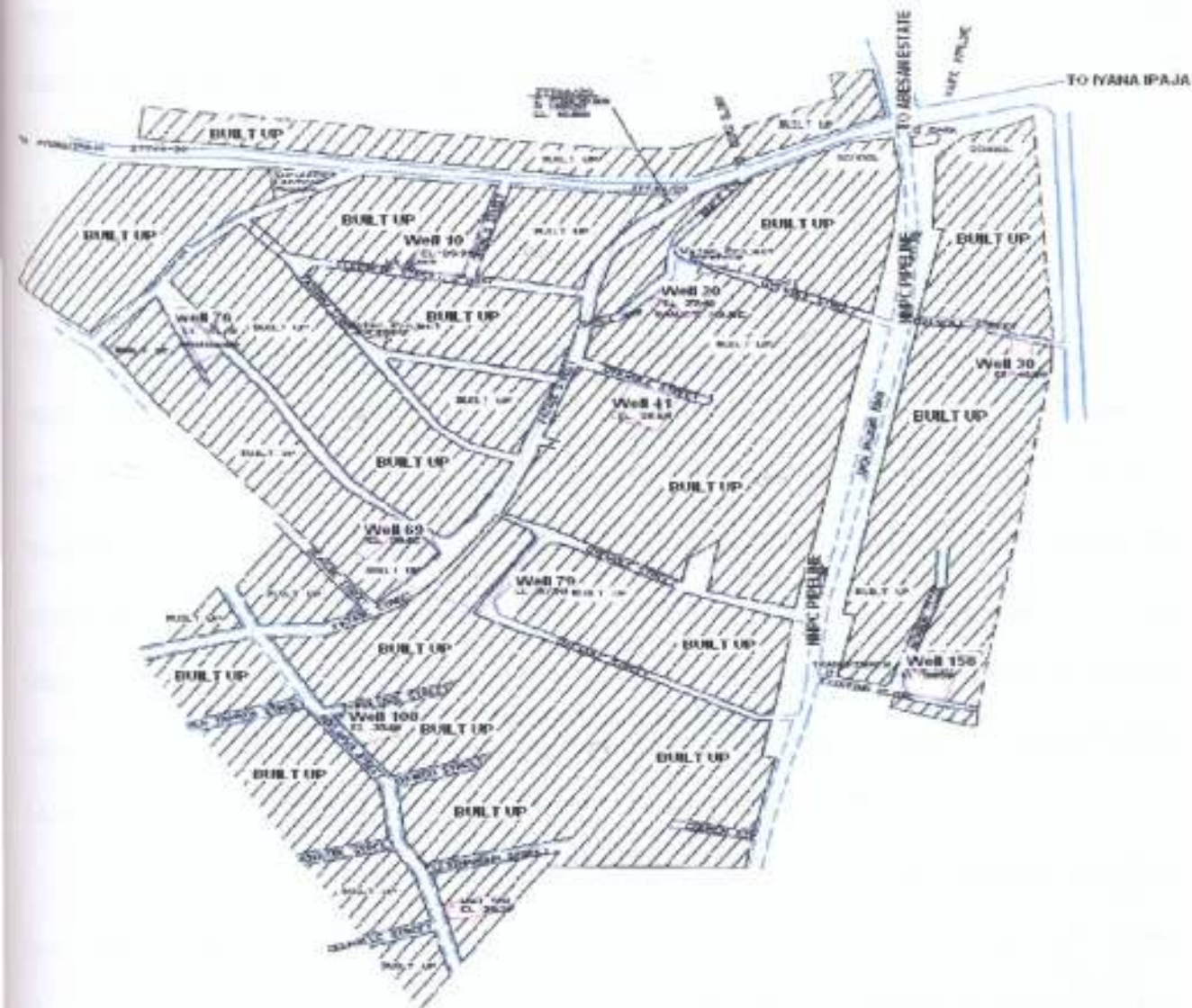


Figure 3.3: Layout of Baruwa community showing NNPC pipeline in dotted lines

3.3.2 Preliminary site reconnaissance and desktop review

Preliminary reconnaissance was carried out to know the environmental settings and hydrological conditions of the site and to confirm information supplied about the site. During the exercise, the actual location of the whole site was verified with the information provided. Adekunle (2008) has prepared an inventory of One hundred and sixty seven (167) existing contaminated wells in this community. The existing contaminated wells with tagged names of the owner were confirmed to correspond with the list issued. Most wells were out of use due to poor water quality as a result of petroleum hydrocarbon contamination. The reconnaissance included gathering existing information from the Nigerian National Petroleum Corporation (NNPC) and the Baruwa

community. These are, geology and soils reports, well records, historical record of pipeline installation/maintenance, historical record of leakage/assessment and depth of pipeline burial.

3.3.3 Geographical setting

Baruwa is a community located in Alimoso Local Government Area in the suburb part of Lagos State. It is situated in South Western part of Nigeria and it lies on latitude $06^{\circ} 35' 12''$ North of the equator and longitude $03^{\circ} 16' 21''$ East of Greenwich meridian (Figure 3.4 and 3.5). It is about 3km away from well-populated Iyana Ipaja along Lagos-Abeokuta expressway and it is predominantly a residential community. The height above the sea level is about 42 meters (Altitude 141 feet). The neighboring town near the community to the East is Kadara and Akinogun, while Fatade and Oduwale are to the South. The surface topography of the area is a rolling terrain and the conceptualized geology underlying this site is reddish brown lateritic coarse, medium to fine SAND, and some grayish sandy CLAY.

The study area has an abundant rainfall of over 2,000 millimeters and southwest wind that blows most of the year. The rainy season lasts from March to October. The dwellers' major source of water is the hand-dug well, which was contaminated with petroleum hydrocarbon between 1994 and 1996. This was as a result of pipeline leakages, which spread over the groundwater of the whole community. These have significant effect on almost all the wells in the site which exhibit very large concentration of petroleum product.



Figure 3.4: Map of Nigeria showing Baruwa, Lagos, Nigeria (Microsoft Encarta Encyclopedia 2004)



Figure 3.5 Zoom-in on Lagos showing Baruwa (Microsoft Encarta Encyclopedia 2004)

3.3.4 Community population and occupation

Baruwa community is basically a residential setting, with over 90,000 people. The residents engage in various activities such as farming, trading, fishing, teaching etc. as a means of livelihood. All living things depend on water for their survival. People within the locality depend on the groundwater for their survival and the soil for the farming activities. Years back, the first people to settle in Baruwa Community engaged in cash crops and peasant farming on the area of land that spread on over 100,000 acres. Then, farming was the predominant activity. As the population increased, some sectors like industries, factories, gasoline storage stations were added to the community.

3.3.5 Site characterization, sampling and testing programme

Detailed field site characterization for the Baruwa site was done by Adekunle (2008) and other postgraduate students. This includes, terrain/ground level elevation mapping and contouring, groundwater level mapping and contouring, detailed hydrostratigraphy, borehole logs/profiling (soil classes), quantifying physical/hydraulic parameters (Hydraulic conductivity/Transmissivity, Stratigraphy/lithology, Porosity, Soil densities, Soil fraction of organic carbon f_{oc} and Grain Size Distribution).

In order to monitor petroleum hydrocarbon transport and natural attenuation in the Baruwa subsurface soil, field assistants were used to carry out periodic sampling and chemical analysis of groundwater and soil samples for twenty-five different wells, spread over the entire Baruwa site. The two sampling sessions took place in, September 2006, and December 2006.

The periodic sampling and analysis for organics (Petroleum hydrocarbon) and inorganics (Terminal electron acceptors) included; Organics Analysis (Total Petroleum Hydrocarbon TPH, Benzene, Toluene, Ethyl Benzene & Xylene BTEX, Methane CH_4), Inorganic Analysis (pH, Conductivity, Dissolved Oxygen DO, Nitrate NO_3^- , Sulphate SO_4^{2-} , Iron Fe, Manganese Mn.), and Contouring/Isoconcentration mapping for contaminant plume description. The samples were

transported to the Multi-Environmental Laboratory, Ketu, Lagos for both organic and inorganic analyses. Details of the laboratory testing procedure for chemical analysis are presented in section

3.4

3.3.6 Collection of soil samples

Soil samples were collected according to the guidance manual on sampling, analysis, and data management for contaminated sites in Canada (CCME 1993, MOEE 1993). The soil samples were scooped into covered glass bottles. Soil samples were scooped from the walls of the existing wells for the first and second sampling sessions.

3.3.7 Collection of water samples

Water samples were collected according to the guidance manual on sampling, analysis, and data management for contaminated sites in Canada (CCME 1993, MOEE 1993). The water samples were collected using 40ml glass vials from the twenty-five monitoring wells using a bailer for the first and second periodic sampling sessions. The water sample depth of collection depended on the depth to water table for the wells, which range from 23-24 meters.

3.3.8 Sample handling and preservation

Care was taken to ensure that sample containers were free of contaminants. Each soil and water sample was properly labeled to avoid mix-up, sealed and preserved with ice-block at the site before taking it to the refrigerator at the laboratory to maintain a temperature less than four degrees centigrade ($<4^{\circ}\text{C}$). Some microbiological activity occurs at this temperature; therefore the possibility of breakdown of the organics exists.

Sample container and sampler were rinsed with distilled water prior to use. Each soil or groundwater sample was properly labeled, sealed and preserved in a big iced cooler. The samples were taken to the laboratory for analysis immediately.

3.3.9 Analysis of soil and water samples

The soil samples collected were analyzed and tested to determine TPH, BTEX, Iron (II), Manganese, Nitrate, sulphide and dissolved oxygen. Ferrous Iron (Fe total) and Manganese analysis was done with the Inductively Coupled Plasma Emission Spectrometry apparatus (see Plate 3.2). TPH and BTEX analyses were carried out by using Gas Chromatography apparatus with flame ionization detector (GC-FID) [(GC) HP5890, powered with HPCHEM software] with a headspace sampler and other apparatus (see Plate 3.3). The water samples collected were analyzed and tested to determine TPH, BTEX, Iron (II), Manganese, Nitrate, sulphide and dissolved oxygen.

3.4 Laboratory Procedures

3.4.1 Determination of metal ions in water and soil samples

This was done at the Multi-Environmental Laboratory, Ketu, Lagos. Water samples were analyzed directly after the filtration through the filter paper into a pre-cleaned glass container using the Inductively Coupled Plasma Emission Spectrometry apparatus. Soil samples were digested with concentrated nitric acid in the fume cupboard, cooled and later filtered in the pre-cleaned container.

Calibration and analysis

Single elemental working standard solutions were prepared by dilution of 1000mg/L stock solution of the individual elements (Mn and Fe). A minimum of five standard working solutions were prepared from the stock solutions which range from 0.1 mg/L to 10.0mg/L. External calibration was performed by running deionized water and a series of calibration standards for each element. The calibration curve was then generated for each of the metal ions.



Plate 3.2: Inductively Coupled Plasma Emission Spectrometry for Metal Analysis (Multi-Environmental Laboratory, Ketu, Lagos)

3.4.2 Determination of dissolved oxygen in water samples

This was done at the Multi-Environmental Laboratory, Ketu, Lagos.

Procedure:- Transferring of the sample to a BOD Bottle, with care being taken to minimize exposure to air. Using of a tube to introduce the water to the bottom of the bottle was done carefully and the removal of the tube slowly while the bottle was overflowing. Addition of 2ml of MnSO_4 reagent with a dropper, discharge the reagent well below the surface. Similarly, introduction of 2ml of sodium Azide solution, followed by 2ml of the KI/NaOH solution was carried out. In each case the tip of the pipette was 2-5cm below the neck of the bottle so that the 2ml quantities were discharged directly into the bulk of the content.

Placement of the stopper in the bottle was done, with no air entrapping. The bottle was inverted to distribute the precipitate uniformly. Then 1ml of concentrated H_2SO_4 was introduced well below the surface and the precipitate was allowed to dissolve. Sample that had been acidified was poured into a 500ml conical flask, titrated with 0.025N $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ until the iodine colour became faint.

Then 5ml of starch indicator was introduced and titration continued until the blue colour was discharged.

3.4.3 Determination of total petroleum hydrocarbon content of water and soil samples

This was done at the Multi-Environmental Laboratory, Ketu, Lagos.

Sample extraction

Water:- Separating funnel was used for the extraction of 1.0 litre of the homogenized water sample with the mixture of the hexane and methylene chloride in the extractable ratio. The extraction was repeated on the same sample for complete solvent extraction. Collected filtrate was cleaned up by using the silica gel and kept for Gas chromatography analysis.

Soil: 5.0g of the homogenized soil sample was weighed into a clean beaker and then extracted with the appropriate mixture of hexane/methylene chloride. The mixture was filtered into a clean beaker by using the appropriate filter paper. Collected filtrate was cleaned up by using the silica gel and kept for Gas chromatography analysis.

3.4.4 Determination of BTEX in water and soil samples

This was done at the Multi-Environmental Laboratory, Ketu, Lagos.

Procedure: Ten (10) ml of water sample were transferred into headspace sampling vial seal and into the headspace sampler for analysis. Also, 10.0g of soil samples were transferred into the sampling vial seal and transferred into the headspace sample for analysis.

The chromatography was electronically integrated and peak area obtained for a particular BTEX component. A calibration curve was made of concentration against peak area and a response factor obtained for each component.



Plate 3.3: Gas Chromatography Apparatus (Multi-Environmental Laboratory, Ketu, Lagos)

3.4.5 Determination of ammonium nitrogen in water samples

This was done at the Multi-Environmental Laboratory, Ketu, Lagos.

Procedure: Ten (10) ml of sample were Pipetted into a 25 ml volumetric flask. Six (6)ml of potassium sodium tartrate, two(2) ml of alkaline sodium phenate solution, two(2)ml of sodium hypochlorite solution and distilled water were added to make up the volume and mixed thoroughly with the content. The absorbance value of the solution was then determined at 630nm on Unicam 5625 Spectrometer. Working standard solutions: standard solution 0,1,2,3,4 and 5ppm were prepared from the 100ppm into 100ml volumetric flasks by diluting appropriate volume with de-ionized water. The absorbance values of the standard solutions were also determined at 630nm on the Spectrometer. This was then used to plot a calibration curve which was used to determine the concentration of ammonium nitrogen in the water sample.

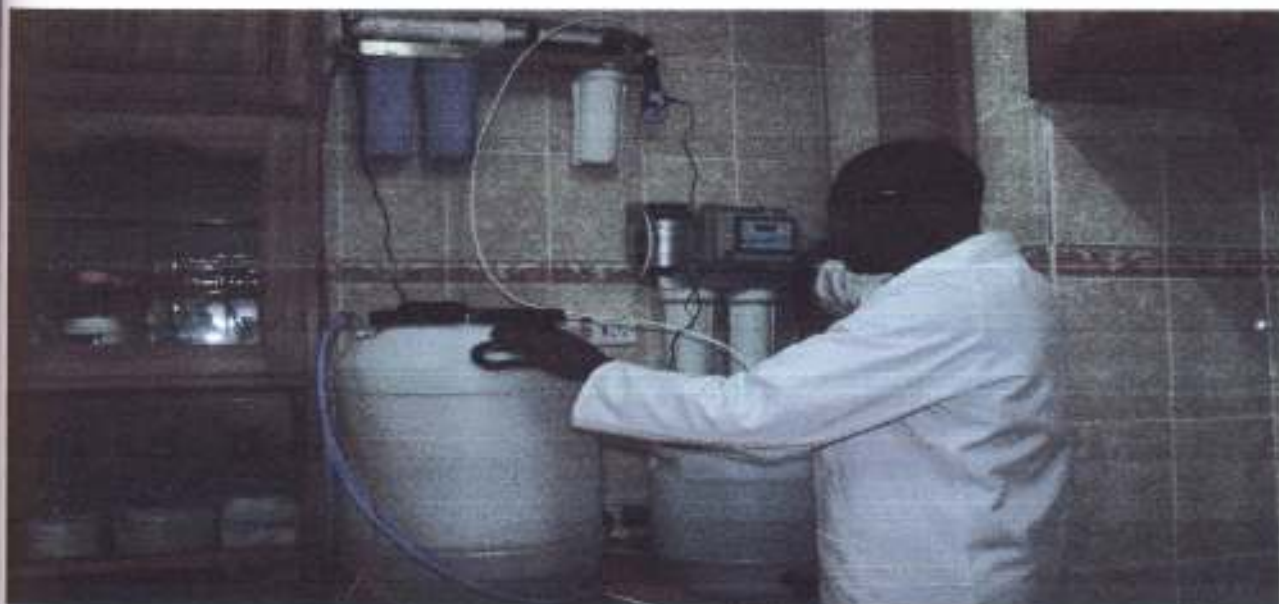


Plate 3.4: Water Purification System (Multi-Environmental Laboratory, Ketu, Lagos)

3.4.6 Determination of sulphide in water samples

Procedure: Samples were treated with sulphide anti oxidant buffer (SAOB). Sulphide ion was measured potentiometrically using a sulphide ion selective electrode in conjunction with a double-junction sleeve type reference electrode. Potentials were read using PH meter of expanded millivolt scale.

3.4.7 Sampling methodology/quality control

The sampling tools and samples were decontaminated prior to and between use as contamination from sampling equipment may contribute significant errors to experimental results. During sample collection cross-contamination may results from poor equipment and apparatus handling or the use of preservatives.

The quality control measures used include (1) written field sampling protocol (2) Decontamination procedures (3) Instrument calibration (4) The preparation and analysis of trip blanks (5) Equipment Blanks (6) Duplicate sampling and holding time for sampling analysis.

3.5 Contaminant Fate and Transport Modeling/Remedial Feasibility Design

The computer program package used for the numerical model was the field-scale *SandModel*. It is a groundwater flow and solute transport simulation package developed during this research. Field-scale *SandModel* is a three-dimensional numerical model describing subsurface flow and solute transport. A field-scale model domain (700 m x 900 m) was discretized using finite difference grid pattern together with field site boundary conditions for the field-scale simulations. *SandModel* is a unique and ideal tool to simulate the movement of water and solutes within the porous media in a realistic, physically-based manner. The field-scale *SandModel* code was used to model groundwater flow, and transport of organic contaminants [i.e., benzene, toluene, ethylbenzene and xylene (BTEX)] in the subsurface of the study area. The numerical model was used to study the conceptual model of the study area. Life-cycle system and a combination of several remedial options in dealing with various stages of contaminant concentration, has been proposed as the approach to remediating this site.

THEORETICAL BACKGROUND

4.1 Fundamental principles

Groundwater flow in a porous medium is described by Darcy's law, which defines a proportionality between the vector of specific discharge, (q) and the gradient of piezometric heads, ∇h :

$$q = -K \nabla h \quad (4.1)$$

where K denotes the tensor of hydraulic conductivity. Dividing the specific discharge, (q) by the transport effective porosity (n_e) yields the flow velocity (v). Combining Darcy's law with the equation of mass conservation results in the groundwater flow equation (Walton, 1991):

$$S_s \frac{\partial h}{\partial t} = \nabla(K \nabla h) + q_s \quad (4.2)$$

S_s is the specific storage coefficient, h is the hydraulic head and q_s is a source/sink term. The solution of the flow equation provides the velocity field, which is a prerequisite for describing the transport of solute compounds.

4.2 Hydrodynamic processes

When considering a conservative, (i.e. non-sorbing and non-degrading compound) a decrease in concentration with increasing distance from the contaminant source is observed. Advection and dispersion cause a spreading and dilution of the plume, which results in diminished concentrations, but not in a diminished mass flux. In this sense, the hydrodynamic processes advection and dispersion do not act as intrinsic attenuation processes, although dispersion is listed in the US EPA definition of natural attenuation (US EPA, 1999).

Spatial variability of advection caused by varying conductivities, porosities and/or aquifer geometries leads to a spreading of the plume (see Figure 4.1 a & b). This is also referred to as large-scale dispersion or macro-dispersion (Dagan, 1988; Dagan, 1990; Cirpka and Kitanidis, 2000). Besides the spreading of a plume, Kitanidis (1994) defines dilution as the increase of volume

occupied by a compound, caused by local-scale dispersion (see Figure 4.1c). Considering a conservative compound, dilution is then the only process that allows mixing between two plumes, i.e. different flow paths. The local-scale dispersion is caused by varying pore size, tortuosity and varying local velocities in a pore due to friction in the pore throat as well as molecular diffusion (Wiedemeier et al., 1999). Cirpka and Kitanidis (2000) show, that the second central moment of a locally measured breakthrough curve gives a measure for the dilution, (i.e. local-scale dispersion) that is not affected by macro-dispersion.

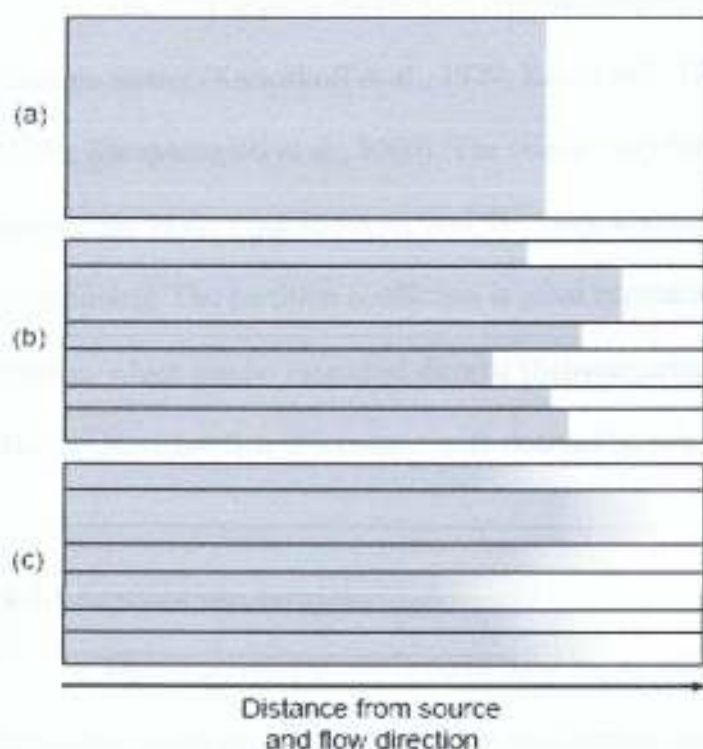


Figure 4.1: Schematic illustration of the effects of macro-dispersion and local-scale dispersion on plume migration. (a) advective transport in a hydraulically homogeneous aquifer. (b) advective transport in a hydraulically heterogeneous aquifer causing macro-dispersion. (c) advective-dispersive transport in a hydraulically heterogeneous aquifer (neglecting transverse dispersion). (Dagan, 1988)

4.3 Sorption of hydrocarbons

The saturated zone of an aquifer represents a two-phase system with the porous medium as solid phase and the flowing groundwater as aqueous phase. The interactions of the organic contaminant

and these two phases depend on the physico-chemical properties of the compound, (i.e. water solubility and vapour pressure) as well as on the geochemical characteristics of the aquifer material. The dominant sorption mechanism of non-ionic organic compounds is the relatively weak "hydrophobic bonding" (Pignatello, 1989; Grathwohl, 1998). Dissolved hydrophobic organic compounds are surrounded by structured water. Bonding onto the solid phase requires less structured water, i.e. entropy increases. Sorbing on the solid phase is thus the thermodynamically favourable process.

The hydrophobic bonding of organic compounds depends directly on the content of soil organic matter (Karickhoff et al., 1979; Karickhoff, 1984; Grathwohl, 1990; Kleineidam et al., 1999; Karapanagioti et al., 2000). The relationship between the concentration of the sorbed compound in the organic matter and the concentration in the solute phase is referred to as partitioning. The partition coefficient is often expressed as a function of the content of organic carbon, which can be measured directly (Schwarzenbach et al., 1993; Grathwohl, 1998). Generally, the partition coefficient increases with decreasing solubility of the considered compound.

4.3.1 Equilibrium sorption

The sorptive uptake of a compound by the solid phase depends on the contaminant concentration in the aqueous phase. In the simplest case, the relationship between sorbed and solute concentration, the so-called isotherm, is linear (see Figure 4.2):

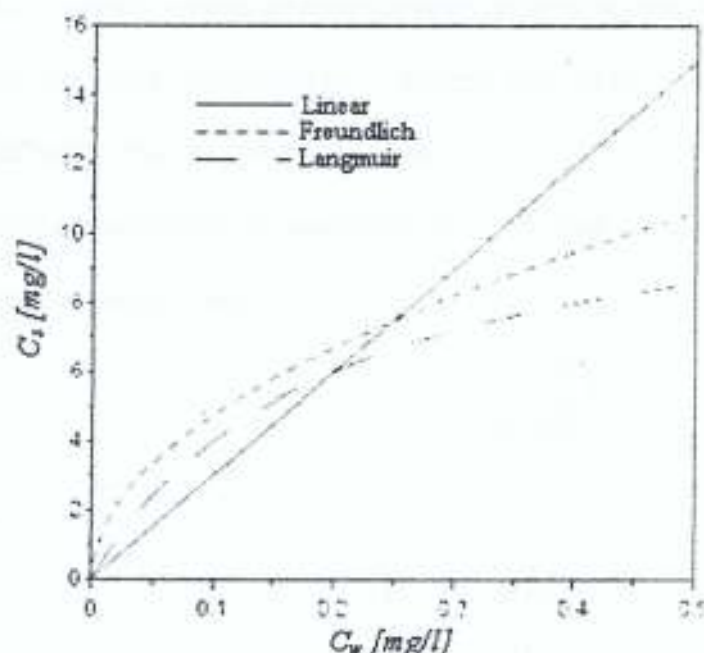


Figure 4.2: Examples of different sorption isotherm models. (Linear: $K_d=30 \text{ L kg}^{-1}$; Freundlich: $K_{fr}=15 \text{ (L kg}^{-1})^{0.5}$ and $1/nfr=0.5$; Langmuir: $K_L=5 \text{ L kg}^{-1}$ and $C_{s, \max}=12 \text{ mg kg}^{-1}$). (Grathwohl, 1998)

$$C_s = K_d \cdot C_w \quad (4.3)$$

where C_s and K_d are the concentration in the solid phase and the distribution coefficient, respectively. However, often a decrease in the sorptive uptake with increasing solute concentrations is observed. Various non-linear isotherm models have been established (see Figure 4.2), like the Freundlich isotherm (Schwarzenbach et al., 1993):

$$C_s = K_{fr} \cdot C_w^{\frac{1}{nfr}} \quad (4.4)$$

or the Langmuir isotherm

$$C_s = \frac{K_L C_{s, \max} C_w}{1 + K_L C_w} \quad (4.5)$$

where K_{fr} and $1/nfr$ denote the Freundlich coefficient and Freundlich exponent, respectively. Correspondingly, K_L is the Langmuir coefficient and $C_{s, \max}$ the maximum sorbed concentration in the solid phase.

All isotherm models assume an instantaneous sorptive uptake of the solvent by the sorbent.

Therefore, the solute concentration C_w in eqns. (4.3) to (4.5) is assumed to be in equilibrium with the sorbed concentration in the solid phase.

As a consequence, the retardation factor R does not explicitly depend on time and is given by (Zheng and Wang, 1998):

$$R = 1 + \frac{\rho}{n_e} \frac{\partial C_s}{\partial C_w} \quad (4.6)$$

with

$$\rho = (1 - n)d_s \quad (4.7)$$

where ρ and d_s denote the bulk density and the density of the solid, respectively. n represents the total porosity. In the case of a linear isotherm, $\frac{\partial C_s}{\partial C_w}$ in eq. (4.6) equals K_d .

4.3.2 Kinetic sorption

Depending on the properties of the organic contaminant and the aquifer material, it might take days to years until sorption/desorption equilibrium between the aqueous and the solid phase is reached. Due to this effect, sorption might seem irreversible, caused by very slow kinetics of the entire desorption process.

Experiments conducted by researchers (Wu and Gschwend, 1986; Ball and Roberts, 1991; Schüth and Grathwohl, 1994) showed, that diffusive transport of the contaminant to the sorbing surfaces causes the observed sorption kinetics. As the majority of the sorbing surfaces is located in the intraparticle pore volume and not on the particle surface, diffusion depends on the particle size and the pore structure (Barber et al., 1992; Kleineidam et al., 1999). After diffusive transport into the intraparticle pore volume, sorption is considered to be fast (Pignatello, 1989).

The diffusion of solute compounds into intra-particle pores is mathematically described by Fick's Second Law (Grathwohl, 1998):

$$\frac{\partial C_w}{\partial t} = D_a \left[\frac{\partial^2 C_w}{\partial r^2} + \frac{2}{r} \frac{\partial C_w}{\partial r} \right] \quad (4.8)$$

where r denotes the radius of the idealized spherical particle and D_a the apparent diffusion coefficient. The apparent diffusion coefficient takes into account the effect of an increased mass storage in the pore due to sorbing solvents.

4.4 Biodegradation of hydrocarbons

Biological degradation of organic compounds is the only one of the above mentioned natural attenuation processes, that in fact eliminates contaminants. Several studies have demonstrated the evidence of biodegradation of hydrocarbons in laboratory experiments (Grbic-Galic and Vogel, 1987; Edwards and Grbic-Galic, 1992; Beller et al., 1992; Nielsen and Christensen, 1994; Kelly et al., 1996; Salanitro et al., 1997) as well as at field scale (Acton & Barker, 1992; Borden et al., 1997; Lahvis et al., 1999; Davis et al., 1999; Gieg et al., 1999). According to these authors biodegradability depends on several factors:

- the type of contaminant and its biochemical properties. It appears, that those compounds that have been available for microorganisms in large quantities and for the longest period of time are the most readily degradable. This explains the decreasing degradability from BTEX (naturally occurring hydrocarbon in crude oil) to chlorinated hydrocarbons (anthropogenically produced since approximately one hundred years) and further to methyl tert-butyl ether (MTBE); produced and distributed since approximately 15 years (Wiedemeier et al., 1999; Salanitro et al., 1997);
- the bioavailability of the hydrocarbon. Only dissolved and, to a limited extent, sorbed compounds are subject to biodegradation (Alexander, 1999; Wiedemeier et al., 1999); and
- the geochemical conditions in the aquifer, like redox conditions, availability of electron acceptors and pH (Christensen et al., 2000; Alexander, 1999; Mormile et al., 1994; Edwards and Grbic-Galic, 1992; Beller et al., 1992).

Salanitro et al. (1997) showed, that biodegradation is less dependent on nutrient growth stimulants (like NH_3 and PO_4^{3-}), soil properties and microbial populations than on the aforementioned factors. Biodegradation proceeds in the following generalized reaction pathway, if the organic compound serves as primary growth substrate (Wiedemeier et al., 1999):



where ED and EA denote electron donor and electron acceptor, respectively.

Based on eq. (4.9), three main types of degradation mechanisms can be distinguished (Alexander, 1999; Wiedemeier et al., 1999):

- biological reduction of organic compounds that act as EA, also referred to as halo-respiration. It is the main mechanism active in the degradation of chlorinated solvents.
- biological oxidation of organic compounds that serve as ED, which most of (not-chlorinated) hydrocarbons are subjected to, like mono-aromatic and aliphatic hydrocarbons.
- methanogenesis as a fermentation process, where organic compounds act as both EA and ED.

Several mathematical models exist to describe biodegradation kinetics. One of the most used models besides first-order decay is the Monod model that accounts for growth of the microbial populations (Alexander, 1999). However, this more sophisticated way of describing biodegradation suffers from the larger number of parameters needed, which cannot be determined directly by laboratory experiments and thus have to be determined by fitting model results to experimental data (Schirmer et al., 1999).

4.4.1 Aerobic degradation of hydrocarbons

During aerobic degradation, microorganisms use free dissolved oxygen as electron acceptor for the pathway described in eq. (4.9). Studies have shown, that almost all petroleum hydrocarbons biodegrade under aerobic conditions (Alvarez and Vogel, 1991; Nielsen and Christensen, 1994; Kelly et al., 1996; Borden et al., 1997). Unless the oxygen is not consumed, the reaction is observed to be very fast. Howard et al. (1991) collected and estimated aerobic half-lives of environmental

pollutants, that range from 3 to 28 days for the BTEX compounds, with ethyl-benzene being the most degradable compound and the xylenes the most recalcitrant ones. Nielsen and Christensen (1994) investigated the variability of aerobic degradation in laboratory experiments. They studied biodegradation in microcosms from different sampling locations within the same aquifer. Degradation rates for BTEX compounds varied within a factor of six for the individual sampling locations.

Due to the low solubility of oxygen in water and the only modest oxygen supply to a plume due to diffusion, the degradation capacity based on oxygen is often not high. Wiedemeier et al. (1999) collected data from 38 sites, where the biodegradation capacities for all terminal electron-accepting processes were determined. The average degradation capacity for oxygen related degradation was quantified to be 3 % of the total degradation capacity.

4.4.2 Anaerobic degradation of hydrocarbons

After oxygen depletion, anaerobic conditions determine the microbial activities. For long times, anaerobic degradation of aromatic hydrocarbons was regarded as non-existent, very slow or incomplete (Wiedemeier et al., 1999). During the last ten to fifteen years, anaerobic degradation of aromatic compounds became an important research area, and several studies (Zeyer et al., 1986; Grbic-Galic and Vogel, 1987; Acton and Barker, 1992; Edwards and Grbic-Galic, 1992; Beller et al., 1992; Lovley et al., 1996) revealed complete mineralization mainly of BTEX compounds under various anaerobic conditions. A general review on anaerobic transformation processes is given by Berry et al. (1987).

Environmental conditions and microbial competition determine, which anaerobic degradation process dominates. Typically, after oxygen depletion, the following sequence of electron acceptors is observed to degrade hydrocarbons:



Half-lives of BTEX compounds under anaerobic conditions are reported to be higher than under

aerobic conditions, and show a high variability (Howard et al., 1991; Edwards and Grbic-Galic, 1992; Davis et al., 1999; Schirmer et al., 1999; Wiedemeier et al., 1999). Some authors also observed benzene remaining recalcitrant under certain conditions (Acton and Barker, 1992; Davis et al., 1999; Thornton et al., 2000).

Even though anaerobic degradation occurs slower than aerobic degradation, at most sites anaerobic degradation plays the major role due to the larger occurrence of nitrate, iron and sulphate in comparison to oxygen. The average anaerobic degradation capacity of 38 sites was determined by Wiedemeier et al. (1999) with 81 % of the overall degradation capacity. Sulphate reduction contributes 86 % (the major part) to the total anaerobic degradation capacity, followed by denitrification (11 %) and iron reduction (3 %).

4.4.3 Methanogenesis

If all electron acceptors mentioned in Sections 4.4.1 and 4.4.2 are depleted, methanogenesis can take place. Then, hydrocarbons act as both electron acceptor and donor (Wiedemeier et al., 1999; Acton and Barker, 1992; Grbic-Galic and Vogel, 1987). Methanogenesis is a two-step process: first, hydrocarbons are fermented to by-products like acetate and hydrogen. In the second step, acetate and hydrogen together with carbon dioxide are utilized by different microorganisms to produce methane, carbon dioxide, and water (Chapelle, 1993).

The described reactions only occur under strongly reducing conditions (hydrogen concentrations greater than 5 nmol L^{-1}) and if carbon dioxide is present. While the process of methanogenesis is thermodynamically not as favourable as the above mentioned reactions, its contribution to the overall degradation capacity was quantified to 16 % (Wiedemeier et al., 1999).

4.5 Advective-Dispersive transport

The advective-dispersive transport equation describes the transport of a solute (a miscible contaminant or tracer) through a groundwater system. Like the fluid continuity equation, it is based

the principle of mass conservation, which equates the change in the mass passing through an elementary block to the change in the mass stored in the block. However, since solutes in general can also react or undergo chemical transformations, we must include a term allowing for reactive changes. The principle of mass conservation therefore becomes:

$$\begin{aligned}
 & -\text{divergence (mass flux)} + \text{time rate of change (reactions)} \\
 & = \text{time rate of change (mass stored)}
 \end{aligned}$$

The most important processes playing a role in the transport of solutes in groundwater (Freeze and Cherry, 1979, Domenico and Schwartz, 1990) are:

Advection: the process whereby the solute is carried by the average groundwater motion through the porous medium;

Mechanical dispersion: the process that causes variations from the average transport pathway on account of the tortuous structure of the pore space of natural porous media;

Diffusion: the net result of the average molecular motion of the solute molecules in the pore water;

Sorption: the process whereby solute molecules attach themselves to the surfaces of soil grains;

Decay: radioactive or biological processes that transform the solute into other substances.

We will here assume that the fluid is essentially incompressible, that the medium does not deform, that isothermal conditions prevail, and that both the dissolved and adsorbed phases decay. We will, for the time being, exclude internal sources or sinks.

On the basis of the above processes, we can write the principle of mass conservation as:

$$\begin{aligned}
 & -\text{divergence (advective mass flux} + \text{dispersive mass flux} + \text{diffusive mass flux)} \\
 & - \text{time rate of change due to decay (solute mass} + \text{sorbed mass)} \\
 & = \text{time rate of change (solute mass stored} + \text{sorbed mass stored)}
 \end{aligned}$$

Designating the advective, dispersive, and diffusive mass fluxes by $\mathbf{J}_v$, $\mathbf{J}_m$, and $\mathbf{J}_d$, respectively, and the solute mass and sorbed mass by M_e and M_s , respectively, we can cast this equation in mathematical form:

$$-\text{div}(\mathbf{J}_v + \mathbf{J}_m + \mathbf{J}_d) + \frac{\partial}{\partial t}(M_e + M_s)_{\text{decay}} = \frac{\partial}{\partial t}(M_e + M_s)_{\text{storage}} \quad (4.10)$$

The solute mass M_e can be represented by the concentration c (solute mass per unit volume of solution, M/L^3). The sorbed mass M_s is generally measured as sorbed mass per mass of solid grain mass, or M/M . In order to make the dimensions compatible, we multiply the sorbed mass by the porous medium bulk density and divide by the porosity,

$$M_s = \frac{\rho_b}{n} s \quad (4.10a)$$

where s is the sorbed mass with respect to the pore volume. The dimension of M_s is $\left(\frac{M}{L^3}\right)$

The advective mass flux is the solute mass carried through the pore space by the average groundwater velocity:

$$\mathbf{J}_v = nc\mathbf{v} \quad (4.10b)$$

The dispersive mass flux represents the combined effect (see Figure 4.3) of variations of the velocity within the pore, variations in the pore size and structure (solute particles will move faster through the larger pores), as well as spreading in the transverse direction (pathways in the tortuous pore network will diverge laterally from the average flow direction). It is generally accepted that the net result is a process that is analogous to molecular diffusion. Thus the dispersive flux is expressed in the form of Fick's law of diffusion.

(a)



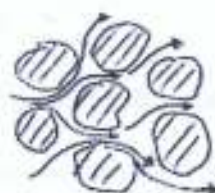
variations of "local" velocity
across a pore

(b)



variations of local velocity
due to spatial variations in
pore size

(c)



Branching of pore channels
due to presence of grains
causing tortuous path or
streamlines

local velocity 'v' tangent to flowline
can vary in direction and magnitude

Figure 4.3: Processes contributing to mechanical dispersion

$$\mathbf{J}_m = -n D_m \nabla C \quad (4.10c)$$

where D_m is the mechanical dispersion tensor, and the net flux is in the direction of the negative concentration gradient.

The diffusive flux is also expressed in the form of Fick's law of diffusion, modified to allow for the fact that molecular diffusion is constrained to the tortuous pore space pathways of the medium:

$$\mathbf{J}_d = -n D_d \tau \nabla C \quad (4.10d)$$

where D_d is the molecular diffusion coefficient in free solution, and τ is the tortuosity tensor (Bear, 1972). Since both the dispersive and the diffusive fluxes have the same form, they are usually combined into a single term. It should be noted, however, that by doing so we implicitly assume that the two processes act at the same spatial scale.

The fully general form of the dispersion tensor in three dimensions is rather complicated for practical use. A brief definition of the dispersion tensor which covers most practical situations is given below:

To present radioactive or biological decay, we assume a first-order reaction of the form:

$$c = c_0 e^{-\lambda t} \quad (4.11)$$

where λ is the decay constant. The decay constant is commonly expressed in terms of the half-life $t_{1/2}$ by writing the above equation at time $t_{1/2}$, which yields:

$$\lambda = \frac{\ln 2}{t_{1/2}} \quad (4.12)$$

The time rate of change due to decay is obtained by differentiation of the decay equation

$$\frac{\partial c}{\partial t} = -c_0 \lambda e^{-\lambda t} = -\lambda c \quad (4.13)$$

Substituting all of the above terms into the solute conservation equation 4.10, we obtain (using summation notation throughout):

$$\frac{\partial}{\partial x_i} \left(-ncv_i + nD_{ij} \frac{\partial c}{\partial x_j} \right) - n\lambda c - \lambda \rho_b s = \frac{\partial(nc)}{\partial t} + \frac{\rho_b}{n} \frac{\partial(ns)}{\partial t} \quad (4.14)$$

If the medium does not deform and the pore space is constant (a reasonable assumption in most contaminant transport scenarios), the porosity n cancels out. If the porosity changes due to solid precipitation, for example, then the more complete form of the equation must be used.

The partitioning between the solute mass and the sorbed mass is usually expressed by means of a functional relationship (Freeze and Cherry, 1979).

A linear reversible partitioning process, under isothermal conditions, is expressed by:

$$s = K_d c \quad (4.15)$$

where K_d is the distribution coefficient. This relationship permits us to write the mass conservation equation all in terms of one variable, c .

The conservation equation now becomes

$$-\frac{\partial}{\partial x_i} (cv_i) + \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j} \right) - \left(1 + \frac{\rho_b}{n} K_d \right) \lambda c = \left(1 + \frac{\rho_b}{n} K_d \right) \frac{\partial c}{\partial t} \quad (4.16)$$

The first term can be expanded and simplified by assuming that no fluid sources or sinks are present; in that case $\frac{\partial v_i}{\partial x_i} = 0$. Further defining the retardation coefficient R as;

$$R = 1 + \frac{\rho b}{n} K_d \quad (4.17)$$

The final advective-dispersive transport equation becomes, in summation form:

$$\frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j} \right) - v_i \frac{\partial c}{\partial x_i} - R \lambda c = R \frac{\partial c}{\partial t} \quad (4.18)$$

or in vector form:

$$\text{div}(\mathbf{D} \nabla \mathbf{c} - \mathbf{v} \mathbf{c}) - R \lambda c = R \frac{\partial c}{\partial t} \quad (4.19)$$

The dispersion tensor $\mathbf{D}$ has a similar form as the hydraulic conductivity tensor $\mathbf{K}$. The components of $\mathbf{D}$ are defined, according to classical theory (Bear, 1972) as;

$$D_{ij} = \alpha_r |v| \delta_{ij} + (\alpha_L - \alpha_T) \frac{v_i v_j}{|v|} + D^* \delta_{ij} \quad (4.20)$$

where α_L and α_T are the longitudinal and transverse dispersivities, respectively, and $D^* = D_d \tau$ is the effective diffusion coefficient in the porous medium, with D_d being the molecular diffusion coefficient in solution and τ the tortuosity of the medium, and δ_{ij} is the Kronecker delta.

For 1-D transport, this equation simplifies to:

$$D = \alpha_L v + D^* \quad (4.21)$$

In two dimensions, the components of the dispersion tensor become:

$$D_{xx} = \alpha_L \frac{v_x^2}{|v|} + \alpha_T \frac{v_y^2}{|v|} + D^* \quad D_{xy} = (\alpha_L - \alpha_T) \frac{v_x v_y}{|v|} \quad D_{yy} = \alpha_T \frac{v_x^2}{|v|} + \alpha_L \frac{v_y^2}{|v|} + D^* \quad (4.21a)$$

In a 2-D coordinate system following the principal directions of the dispersion tensor, which are parallel and perpendicular to the flow lines, these components simplify to:

$$D = \alpha_L v + D^* \quad D_{yy} = \alpha_T v + D^* \quad (4.21b)$$

$$D_{xy} = D_{xx} = D_{yz} = 0 \quad (4.21c)$$

In 3-D systems, there will be one direction of longitudinal dispersion and two directions of transverse dispersion. The classical dispersion theory holds only if the dispersivities in the two transverse directions are the same dispersion in the vertical direction in an aquifer is generally

much smaller than transverse dispersion in the horizontal. For this situation, the components of the 3-D dispersion tensor can be written as (Frind, 2003),

$$\begin{aligned}
 D_{xx} &= \alpha_l \frac{v_x^2}{|v|} + \alpha_{TH} \frac{v_y^2}{|v|} + \alpha_{TV} \frac{v_z^2}{|v|} + D^* & D_{xy} &= D_{yx} = (\alpha_l - \alpha_{TH}) \frac{v_x v_y}{|v|} \\
 D_{yy} &= \alpha_l \frac{v_y^2}{|v|} + \alpha_{TH} \frac{v_x^2}{|v|} + \alpha_{TV} \frac{v_z^2}{|v|} + D^* & D_{xz} &= D_{zx} = (\alpha_l - \alpha_{TV}) \frac{v_x v_z}{|v|} \\
 D_{zz} &= \alpha_l \frac{v_z^2}{|v|} + \alpha_{TH} \frac{v_x^2}{|v|} + \alpha_{TV} \frac{v_y^2}{|v|} + D^* & D_{yz} &= D_{zy} = (\alpha_l - \alpha_{TV}) \frac{v_y v_z}{|v|}
 \end{aligned} \quad (4.22)$$

4.6 Classical theory of dispersion in a porous medium and the medium's dispersivity

Simple geometrical models of dispersion based on a capillary tube cannot be easily extended to take into account the complex structure of a porous medium's pore structure. This difficulty led to the development of statistical models of dispersion based on random walk theory (Scheidegger, 1954).

Scheidegger (1954) studied the statistics of the motion of a single tracer particle in a homogeneous, isotropic medium. The motion was assumed to comprise of a sequence of elementary displacements with the direction and length of each displacement being random and uncorrelated. By uncorrelated, it was meant that any given displacement step did not depend on the direction or length of the previous step (i.e. the particle had no memory). Scheidegger (1954) found that the random advective displacements led to a Brownian-particle motion. However, because the author assumed an isotropic medium such that the random step size was independent of direction (the same both along and transverse to mean flow direction) D_m was considered to be a scalar. Thus the model predicted an equal amount of spread in all directions.

A major contribution by Scheidegger (1954) was the introduction of the "constant of dispersion" which was called the medium's dispersivity.

$$D_m = \alpha \bar{v} \quad \alpha = \text{dispersivity}$$

Thus, the mechanical dispersion co-efficient was shown to depend linearly on the mean fluid velocity $\bar{v}$, unlike the geometrical models. Scheidegger (1954) argued that the dispersivity is a characteristic of the porous medium.

Following Scheidegger's (1954) work, other statistically-based models were developed by De Josselin De Jong (1958), Saffman (1960) and Dagan (1988). They considered the porous medium to be comprised of a network of interconnected channels with neighbouring random displacements being spatial correlated. They showed theoretically that longitudinal dispersion in the direction of mean flow is greater than the transverse dispersion across the mean flow direction. The ratio of the longitudinal dispersion coefficient to the transverse dispersion coefficient, D_l/D_t , was found to be in the range of 5 to 7. This was consistent with experimental findings. They did not, however, make the relation between D_l and D_t and the medium's dispersivity.

4.7 The Magnitude of the Dispersivity

The classical dispersion theory relates the strength of the mechanical dispersion process to the value of the medium's dispersivity; it does not however provide a functional relationship between α_l or α_t and the statistical properties of the pore space of homogeneous materials or the hydraulic conductivity variations of heterogeneous materials. The values of α_l and α_t have therefore been traditionally obtained by fitting solutions of the advection-dispersion equation to observed concentration patterns.

4.7.1 Results based on homogeneous 1 – D sand columns

From such tests, it is generally observed that

$$10^{-4}m \leq \alpha_l \leq 10^{-2}m$$

with the average diameter of a grain being a typical value. Little work has been done on measuring

α_l , although a few tests suggest that $\frac{\alpha_l}{\alpha_t}$ is on the order of 10 or 20. For small values of α_t , or

small values of v , molecular diffusion may dominate over mechanical dispersion.

Results of such laboratory experiments have been summarized in terms of the peclet number (Freeze and Cherry, 1979):

$$P = \frac{vd}{D_o} = \frac{\text{mechanical mixing}}{\text{molecular diffusion}} \tag{4.23}$$

where d is a characteristic length usually taken to be a mean grain diameter and D_o is the free-solution diffusion coefficient ($\approx 10^{-5} \text{ cm}^2/\text{s}$)

From such column tests, it has been suggested that:

$$D_l = \alpha_l v^m + D_d \tag{4.24}$$

with $1 \leq m \leq 2$. Some experimentalists suggest $m = 1.2$ although in practice one usually assume $m = 1$. The problem with using $m \neq 1$ is that the dimensionality of α_l (supposed to be (L)) is difficult to rationalize (Sudicky, 1986).

4.7.2 Results based on field studies

Dispersivity values based on field studies are typically several orders of magnitude larger than those obtained from laboratory studies performed on homogeneous packings of sand or glass beads. The larger field values are usually attributed to the larger scale velocity variations caused by heterogeneity of the hydraulic conductivity field.

Tracer tests performed in the field can be broadly categorized into three types:

1. Single well tests in which the tracer is pumped in for a short duration and then pumped out with the concentration being monitored during pump-out (forced-advection radial flow).

1. Two-well tracer tests in which tracer is introduced via an injection well and the concentration is monitored at a nearby pumping well (forced advection doublet flow field). Observation wells are sometimes located between the injection and pumping wells.

3. Natural gradient test: The tracer is introduced passively into one or more tracer-release wells for a brief period and the plume is allowed to advect and disperse under natural conditions. The plume is tracked with a network of down-gradient samplers.

It is generally acknowledged that natural gradient tests are more representative and proper instrument will allow dispersion parameter estimation in the three coordinate directions; however, they are more time consuming and expensive to perform than the forced advection type. To date, only a few highly-detailed natural gradient tests have been carried out (Sudicky, 1986, and Freyberg, 1986) for the Borden aquifer and the recent Cape Cod test.

Such field tests indicate that;

$$10^{-2}\text{m} \leq \alpha_l \leq 10^0\text{m}$$

With the smaller values obtained from tests in which the injected plumes "sampled" a few units to a few tens of m^3 of aquifer and the larger values are from plumes sampled a few hundred to a few thousand of m^3 of aquifer. For example, both the Borden and Cape Cod natural gradient tests performed recently involved travel distances on the order of 100m and larger and both yielded α_L values of about 1.0 m. The Borden aquifer is a weakly to moderately heterogeneous bedded sand deposit and the Cape Cod site is a moderately heterogeneous sand and gravel outwash deposit.

The vertical Transverse dispersion observed at both the Borden and Cape Code sites was observed to be very weak and is on the order of molecular diffusion. This is not unexpected because both aquifers are mainly horizontally bedded with the mean flow direction being along the bedding. Horizontal transverse dispersion was also observed to be much weaker than the longitudinal spreading.

Field-scale dispersivity values have also been obtained by fitting numerical (i.e. finite element or finite difference) models to contaminant plumes emanating from land fills, sewage lagoons etc. These studies have commonly yielded α_l in the range of

$$10^0 \leq \alpha_l \leq 10^2 m$$

With α_l being on the order of 10 to 20 times smaller than α_T . Travel distances on the order of 100's of metres to kilometers are often involved. One should, however, bear in mind that the dispersivities obtained in this way may only be arbitrary curve-fitting parameters unrelated to the structure of the hydraulic conductivity variations in the aquifer if (i) the history of mass input at the source is unknown or poorly defined, (ii) the gross features of the geology, and hence the hydraulic conductivity of hydrogeologic units, are not properly resolved, (iii) the sampling network does not admit proper temporal and spatial resolution of the plume and (iv) possible transients in the nature of the groundwater flow field are ignored.

Recent developments in field-scale dispersion theory based on stochastic representations that make use of statistical parameters characterizing spatial variability of hydraulic conductivity avoid some of the above-mentioned difficulties.

4.8 Initial and Boundary Conditions

In order to solve the advection-dispersion equation, we need to specify some additional information on the dependent variable $c(x, y, z, t)$. That is, what is the value of c throughout the domain at time $t = 0$ and what conditions must c satisfy on the entire boundary for all t .

Initial conditions: - only needed from transient problems.

Specify: $C(x, y, z, t=0) = f(x, y, z)$

4.8.1 Boundary conditions

We have a choice on any portion of the boundary.

Specify C on boundary

- known as 1st type or Dirichlet boundary condition.

2. Specify value of derivative of C normal to boundary (i.e. dispersive flux)

- known as 2nd - type or Neuman boundary condition.

3. Specify both the value of C and its derivative on the boundary.

- known as 3rd - type or mixed or Cauchy boundary condition.

It should be noted that the condition specified on the boundary could also be a function of Time.

A differential equation, such as the advection dispersion equation, plus boundaries

conditions and if necessary, the initial condition constitutes a boundary-value problem.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Investigation of Contaminant Transport and Natural Attenuation in a Tropical Porous Media Soil: Sand Tank Model Design and Evaluation

5.1.1 Groundwater movement

Groundwater moves from areas of higher elevation or higher pressure/hydraulic head (recharge areas) to areas of lower elevation or pressure/hydraulic head. In 1856, Henri Darcy first concluded that velocity of flow through a porous media was directly proportional to the gradient of piezometric head (hydraulic gradient). Darcy's law is also a macroscopic law. For a given cross-sectional area, hydraulic gradient and hydraulic conductivity, it predicts the macroscopic (average) flow rate of water traveling through the soil and does not describe microscopic (actual) velocity of water between the soil grains.

The most important processes playing a role in the transport of solutes in groundwater (Freeze and Cherry, 1979, Domenico and Schwartz, 1990,) are; - advection: the processes whereby the solute is carried by the average groundwater velocity through the porous medium and - mechanical dispersion; the processes that cause variations from the average transport pathway on account of the tortuous structure of the pore space of natural porous media.

Dispersivities are scale dependent with respect to numerical model grids and depend on how explicitly field velocity distribution, and actual geometry of aquifer heterogeneity are simulated in numerical models (Freyberg, 1986). Predictions of future plume migration may require selection of dispersivity values significantly different from calibrated model values. In profile, contaminant migration tends to be concentrated in the more permeable zones of uniformly porous aquifers causing fingerling and irregularity in plumes. However, diffusion from permeable zones into adjacent less permeable zones tends to create more regular plumes as concentrations are reduced in zones of dispersion and advection and concentrations are increased in the zones of lesser flow (Wang *et al*, 2009). In general, dispersivity is directionally dependent on aquifer vertical, and horizontal hydraulic

functional dependent.

5.1.2 Sand tank model

Sand tank model is a physical aquifer model and ever since, early 1980s, it has been widely employed in several fields of study in the laboratory to observe groundwater flow and solute transport.

A three-dimensional physical aquifer model was used to study the dissolution of a dense non-aqueous phase liquid (DNAPL) pool. The model aquifer comprised a packing of homogeneous, medium-sized sand and conveyed steady, unidirectional flow, Dela Barre *et al* (2002)

Ng *et al* (2006) also investigated injection of edible oils into the subsurface. Injection of edible oil into a laboratory sand tank model can provide an effective, low-cost alternative for simulating anaerobic bioremediation processes. However, concerns have been raised about the effects of oil viscosity and variations in aquifer permeability on the final distribution of oil in the subsurface. Three-dimensional (3-D) sandbox experiments (1.2 m x 0.98 m x 0.98 m) were conducted to study the distribution of edible oil emulsions under homogeneous and heterogeneous conditions. A fine emulsion was first injected followed by chase water to distribute the emulsion throughout the sandbox. This approach was very effective, resulting in a reasonably uniform volatile solids distribution in the top, middle, and bottom layers.

Laboratory and numerical modeling investigation were completed to study the unconfined groundwater flow and transport processes near a seepage-face boundary Simpson *et al* (2003). The laboratory observations were made in a radial sand tank and included measurements of the height of seepage-face, flow velocity near the seepage-face, travel time distribution of multiple tracer slugs, and streamlines. The results imply that vertically average flow models that employ Dupuit approximations might introduce error in the analysis of localized solute transport near a seepage-face boundary.

5.1.3 Laboratory sand tank (aquifer) model experimental set-up

Sand tank model as used in this research work is a 3-dimensional physical model apparatus consisting of transparent glass and plexiglass material – which enables an observer to clearly monitor the simulated groundwater flow and solute transport in the laboratory. The model attempts to simulate how groundwater is contaminated and the rate at which the contaminant spreads in the groundwater both longitudinally and transversely. Details of the laboratory sand tank model experimental set-up are in Chapter Three (Section 3.2)

5.1.4 Characterization of the porous media and flow characteristics

5.1.4.1 Characterization of the Owena sand

A measure of the coastal river sand (700 g) was weighed and used in the sieve analysis. After which the various constituents material retained on each sieves were weighed and recorded. The test was conducted in accordance with the BS 1377 (1990). This exercise was repeated for three (3) separate samples taken at random from the river sand. The Owena river sand material is relatively homogeneous medium-to-fine-grained sand. Clay size fractions are almost absent (Table A1[Appendix A1], Figure 5.1).

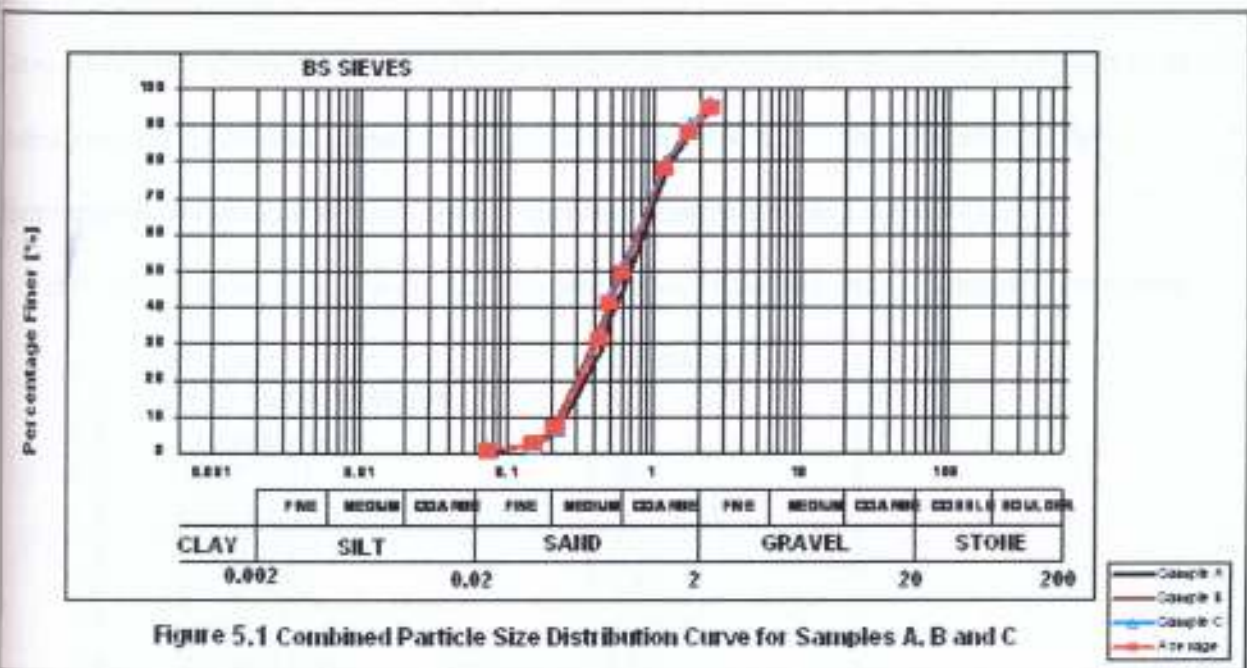


Figure 5.1 Combined Particle Size Distribution Curve for Samples A, B and C

From the graph

Sample A	Sample B	Sample C
$D_{10} = 0.24$	$D_{10} = 0.23$	$D_{10} = 0.24$
$D_{30} = 0.44$	$D_{30} = 0.40$	$D_{30} = 0.45$
$D_{50} = 0.54$	$D_{50} = 0.55$	$D_{50} = 0.56$
$D_{60} = 0.80$	$D_{60} = 0.70$	$D_{60} = 0.70$

Average value of the three samples, A, B, and C

$$D_{10} = \frac{0.24 + 0.23 + 0.24}{3} = 0.24$$

$$D_{30} = \frac{0.44 + 0.4 + 0.45}{3} = 0.43$$

$$D_{50} = \frac{0.54 + 0.55 + 0.56}{3} = 0.55$$

$$D_{60} = \frac{0.8 + 0.7 + 0.7}{3} = 0.73$$

$$\text{Uniformity coefficient } C_u = \frac{D_{60}}{D_{10}} = \frac{0.73}{0.24} = 3.04$$

$$\text{Coefficient of gradation } C_z = \frac{D_{30}^2}{D_{60} \times D_{10}} = \frac{0.43^2}{0.73 \times 0.24} = 0.191$$

The river sand is poorly graded sand (SP).

The results of the characterization of the geotechnical, hydraulic and geochemical properties of the

Owena sand from laboratory analyses are presented in Table 5.2a. The groundwater flow

characteristics of the alluvial sand (Owena sand) are summarized in Tables 5.2b.

Table 5.2a: Estimates of Owena Sand Geotechnical, Hydraulic and Geochemical Properties

	Property	Estimates
1.	Bulk Density (Mg/m^3)	1.9
2.	Porosity (%)	32
3.	WHC (%)	30.2
4.	Hydraulic Conductivity (m/s)	5.76×10^{-4}
5.	pH in Water	7.52
6.	pH in KCL	6.52
7.	Org. C [f_{oc}]	0.0008
8.	Total N (%)	0.03
9.	Av. P (ppm)	6.9
10.	Exc. Ca (me/100g)	0.58
11.	Exc. Mg (me/100g)	0.54
12.	Exc. Na (me/100g)	0.12
13.	Exc. K (me/100g)	0.12

14.	CEC (me/100g)	1.36
15.	B.Sat (%)	87.18

Note: WHC – Water Holding Capacity
 CEC – Cation Exchange Capacity
 Exc. - Exchangable
 B. Sat - Base Saturation
 me - milli equivalent
 f_{oc} - fraction of organic carbon

Table 5.2b: Sand Tank Flow Characteristics

IN	HEAD cm		HEAD DIFFEREN CE (dh) cm	GRADIEN T dh/dl	OUTFLOW RATE (ml/min) ml/min	DISCHAR GE PORTS
	OUTLET	INLET				
1	68.5	73	4.5	0.0321	58	1 ST PORT
2	63.5	73	9.5	0.0679	160	2 ND PORT
3	58.5	73	14.5	0.1036	280	3 RD PORT
4	53.5	73	19.5	0.1393	405	4 TH PORT

= 140 cm (Length of middle chamber)

5.1.4.2 Tracer experiment: experimental procedures

Injection of the Solute Pulse

Table 5.3 summarizes the pertinent information on the non-reactive tracer in the injected solution, including, average concentration, total dissolved mass and the aqueous diffusion coefficient.

Table 5.3: Nonreactive Tracer in the Experimental Injection Solution

Tracer Ion	Av. Concentration (mg/l)	Mass Injected (g)	Aqueous Diffusion Coefficient (m^2/s)*
Chloride (Cl)	12000	12.0	2.03×10^{-9}

*Free ion aqueous diffusion coefficient at 20°C. Taken (source: Cussler, 1984)

An injection system was designed to approach the ideal goal of creating essentially instantaneous and with minimal disturbance of the natural flow field. Three injection wells arranged as indicated in Figure 3.2 were each slotted and screened within the saturated zone, over the vertical interval 0.42- 0.82m below the aquifer model surface. The injection system was designed to provide to each of the injection wells an equal (20 ml) and uniform flow of a solution of uniform composition (12 g/l) [28.1 mS/cm]. Twelve (12.0)g of sodium chloride dissolved in 1000 ml of water was injected into three upgradient injection wells on July 17, 2007. Injection period was 5 minutes. Observation

ls (4 mini wells) were located 40 cm and 80 cm away from the injection wells, in the middle member of the sand tank model.

The chloride conductivity at the observation wells were measured using a Portable Horiba U-10 Water Quality Checker. The measurement interval varied between 1 and 10 hours. A 20 ml syringe and 5 mm diameter Teflon siphon tube was used for collection of the samples into 50 ml plastic bottles. The tester, syringe and the siphon tube were rinsed with distilled water before and after each measurement.

After injection the plume of solute moved under the action of the quasi natural gradient of the sand tank and the elevated water reservoir. Plume movement was monitored using a network of multilevel point samplers. The spatial and temporal distribution of data collected for the tracer is summarized in tables 4 and 5. In all 360 samples were collected during twenty four (24) sampling sessions, for the three days of the tracer experiments in the Sand Tank. Elapsed travel time was 34 hrs, with a maximum travel distance of 0.8 m.

Table 5.4: Spatial and Temporal Distribution of Chloride Conductivity for the Tracer Experiment. (1st Port).

		Conduc- tivity (mS/cm)	Conduc- tivity (mS/cm)	Conduc- tivity (mS/cm)	Conduc- tivity (mS/cm)	Conduc- tivity (mS/cm)		
Sampling Point		A	B	C	D	E	Time after Injection (hours)	Remark
Sample 1	Top	0.286	0.285	0.283	0.285	0.286		Baseline Conductivity
	Middle	0.283	0.286	0.286	0.283	0.284		
	Bottom	0.286	0.284	0.282	0.284	0.286		
Sample 2	Top	26.00	0.580	0.295	0.295	0.289	1.0	
	Middle	26.00	0.560	0.290	0.290	0.289		
	Bottom	26.00	0.560	0.290	0.290	0.289		
Sample 3	Top	12.00	0.732	0.422	0.423	0.328	2.0	
	Middle	12.00	0.720	0.416	0.417	0.324		
	Bottom	12.00	0.721	0.413	0.415	0.322		
Sample 4	Top	4.10	1.523	0.518	0.518	0.467	4.0	
	Middle	4.10	1.521	0.515	0.517	0.468		
	Bottom	4.10	1.516	0.505	0.502	0.468		
Sample 5	Top	3.407	3.142	1.138	1.137	0.833	6.0	
	Middle	3.410	3.150	1.138	1.136	0.834		
	Bottom	3.411	3.105	1.138	1.132	0.837		
Sample 6	Top	2.331	3.800	1.407	1.400	1.320	8.0	
	Middle	2.342	3.808	1.407	1.402	1.320		
	Bottom	2.345	3.821	1.412	1.413	1.325		
Sample 7	Top	1.337	3.202	1.100	1.104	1.522	10.0	
	Middle	1.346	3.206	1.102	1.108	1.523		
	Bottom	1.348	3.215	1.110	1.114	1.528		

Sample 8	Top	0.721	0.840	0.518	0.515	1.506	20.0	
	Middle	0.746	0.850	0.520	0.518	1.508		
	Bottom	0.759	0.860	0.570	0.521	1.512		
Sample 9	Top	0.610	0.675	0.424	0.425	1.235	22.0	
	Middle	0.610	0.680	0.421	0.418	1.236		
	Bottom	0.620	0.680	0.434	0.438	1.236		
Sample 10	Top	0.484	0.522	0.306	0.305	1.043	24.0	
	Middle	0.482	0.532	0.308	0.310	1.046		
	Bottom	0.485	0.528	0.314	0.315	1.048		
Sample 11	Top	0.412	0.463	0.285	0.283	0.901	26.0	
	Middle	0.408	0.472	0.289	0.290	0.902		
	Bottom	0.417	0.472	0.296	0.299	0.905		
Sample 12	Top	0.358	0.381	0.254	0.253	0.748	28.0	
	Middle	0.362	0.383	0.256	0.258	0.751		
	Bottom	0.371	0.385	0.261	0.260	0.753		
Sample 13	Top	0.310	0.346	0.272	0.269	0.556	30.0	
	Middle	0.309	0.348	0.274	0.276	0.558		
	Bottom	0.317	0.348	0.278	0.281	0.567		
Sample 14	Top	0.296	0.286	0.286	0.285	0.391	34.0	
	Middle	0.294	0.286	0.286	0.284	0.398		
	Bottom	0.302	0.290	0.288	0.288	0.402		

Table 5.5: Spatial & Temporal Distribution of Chloride Conductivity for the Tracer Experiment (2nd Port)

		Conductivity (mS/cm)	Conductivity (mS/cm)	Conductivity (mS/cm)	Conductivity (mS/cm)	Conductivity (mS/cm)		
Sampling Point		A	B	C	D	E	Time after Injection (hours)	Remark
Sample 1	Top	0.286	0.285	0.283	0.285	0.286		Baseline Conductivity
	Middle	0.283	0.286	0.286	0.283	0.284		
	Bottom	0.286	0.284	0.282	0.284	0.286		
Sample 2	Top	24.00	0.420	0.300	0.302	0.287	1.0	
	Middle	23.98	0.422	0.300	0.300	0.286		
	Bottom	24.00	0.422	0.302	0.301	0.288		
Sample 3	Top	10.00	0.804	0.402	0.404	0.292	2.0	
	Middle	10.00	0.806	0.402	0.402	0.294		
	Bottom	10.02	0.811	0.408	0.406	0.301		
Sample 4	Top	3.396	1.201	0.813	0.813	0.567	4.0	
	Middle	3.400	1.201	0.815	0.817	0.568		
	Bottom	3.404	1.212	0.815	0.816	0.568		
Sample 5	Top	1.950	2.620	1.101	1.102	0.833	6.0	
	Middle	1.950	2.620	1.100	1.101	0.834		
	Bottom	1.955	2.650	1.102	1.102	0.837		
Sample 6	Top	0.822	2.101	0.782	0.782	1.220	8.0	
	Middle	0.825	2.104	0.786	0.786	1.220		
	Bottom	0.828	2.107	0.792	0.790	1.221		
Sample 7	Top	0.420	1.100	0.581	0.581	1.000	10.0	
	Middle	0.420	1.102	0.584	0.584	1.000		
	Bottom	0.425	1.105	0.592	0.590	1.011		
Sample 8	Top	0.316	0.420	0.409	0.409	0.530	20.0	
	Middle	0.318	0.430	0.410	0.409	0.550		
	Bottom	0.322	0.430	0.412	0.411	0.562		
Sample 9	Top	0.296	0.325	0.288	0.289	0.418	22.0	
	Middle	0.298	0.330	0.290	0.291	0.420		
	Bottom	0.304	0.330	0.290	0.292	0.424		
Sample 10	Top	0.286	0.285	0.283	0.285	0.286	24.0	
	Middle	0.283	0.286	0.286	0.283	0.284		
	Bottom	0.286	0.284	0.282	0.284	0.286		

5.1.5 Results/Overview of plume behavior

The monitoring system consisted of a network of multilevel sampling devices ((Figure 3.2 and Plate 3.1). The horizontal spacing of the multilevel wells varied from 40 cm to 80 cm, while the vertical spacing of the sampling points was 0.20 m. The multilevel samplers were constructed with PVC pipes (12.5 mm diameter). The breakthrough curves were plotted and the statistical moments of the tracer breakthrough curves, were examined throughout the duration of tracer passage.

5.1.5.1 Observation for the multilevel sampling points

The Tracer Breakthrough Curves (TBCs) for twenty four (24) sampling sessions for the two different discharge rates [58ml/min and 160ml/min] used are summarized in Figures 5.2 -5.5. Details of the TBCs are in the Appendix B.

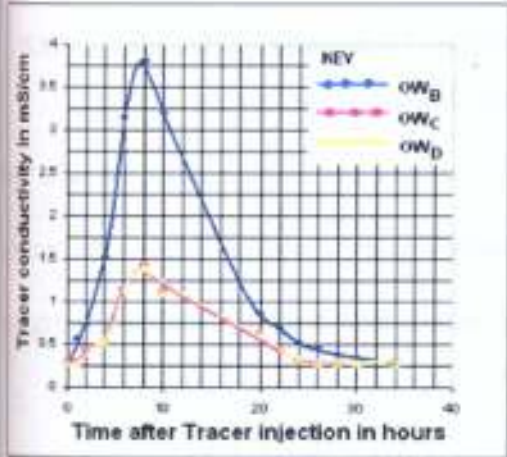


Figure 5.2: TBC for observation wells OW_B, OW_C and OW_D (Discharge Port 1)

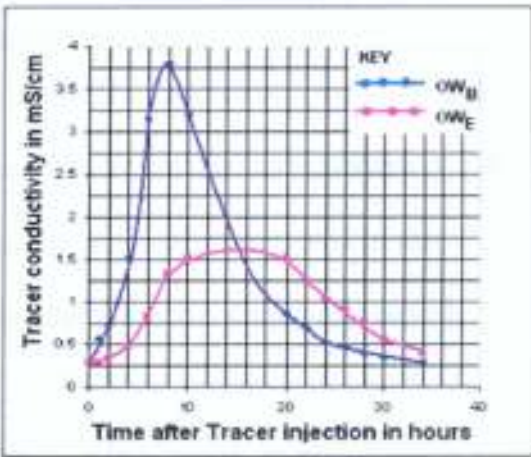


Figure 5.3: TBC for observation wells OW_B and OW_E (Discharge Port 1)

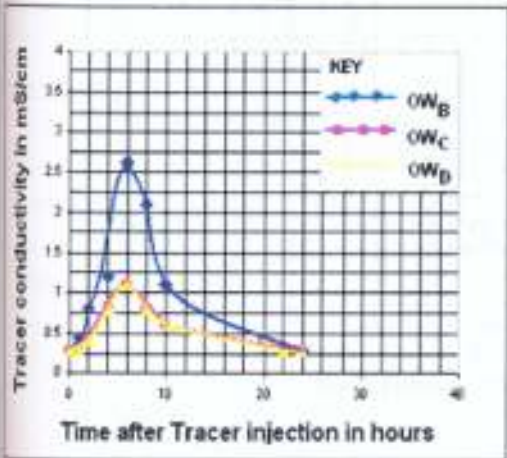


Figure 5.4: TBC for observation wells OW_B, OW_C and OW_D (Discharge Port 2)

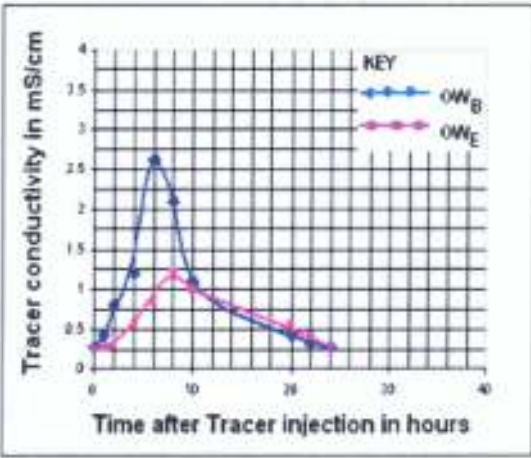


Figure 5.5: TBC for observation wells OW_B and OW_E (Discharge Port 2)

There was no significant difference in the TBC for the top, middle and bottom positions for each of the four locations B,C,D,E. The tracer injection was also over the entire length of the injection well A. This confirms the homogeneity of the porous media material. However, superimposition of the

TBCs for the different locations B,C,D,E, Figures 5.2-5.5, reveal that the centre of mass of the chloride plume is on the central axis along the length of the sand tank, indicated by location B. TBCs for locations C and D which are 12cm each away from the central axis of the tank, show a marked reduced area, and hence solute mass in solution. This also indicates that the longitudinal dispersion is dominant as expected, since this is the direction of flow. For observation wells B and E, Figure 5.3, TBC for location E which is 40cm down stream of location B, the peak is remarkably reduced as a result of plume dilution from the flow of groundwater and the distance from the source. Increased flow of the groundwater (discharge port 2 [160ml/min]), Figures 5.4 and 5.5, has brought about a reduction in the mass of solute in the Sand Tank system, due to the flushing of the tracer with the increased flow of groundwater.

5.1.5.2 Statistical temporal moments of tracer breakthrough curve

The first arrival of the chloride tracer was detected at the first observation well (OW_{BM}), 1 hour after tracer injection (see Figure 5.6). The chloride conductivity reached its maximum of 3.8 mS/cm, after eight (8) hours tracer injection. After 34 hours, the conductivity returned to the background value. The sand tank discharge rate (Port 1) stayed at 58ml/min during this period.

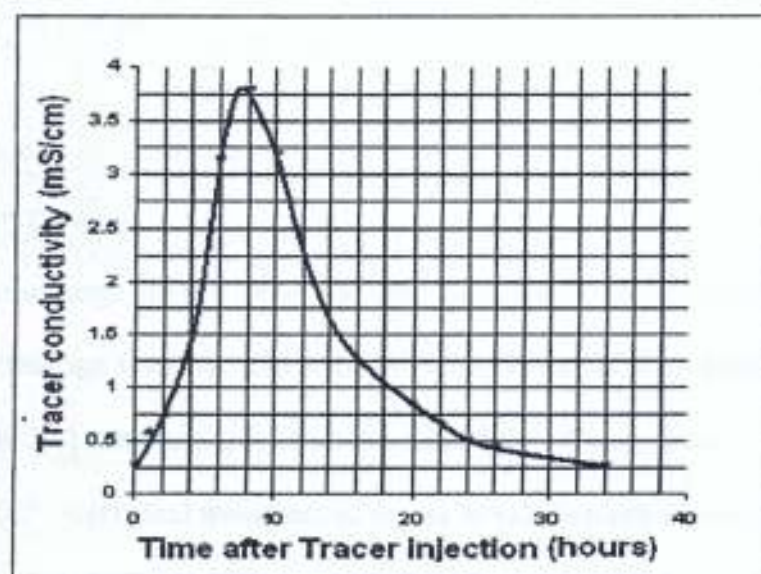


Figure 5.6: Measured Tracer Breakthrough Curve for observation well (OW_{BM}) [Port 1]

The following sections provide a quantitative assessment of a number of aspects of the preceding qualitative description of plume movement using statistical temporal moment estimates. Statistical moments of Tracer Breakthrough Curves, was used to provide quantitative measures of various solute

transport parameters, such as the velocity, dispersion coefficient and dispersivity for the porous media (Freyberg, 1986). This method of statistical moments entails finding the area under the graph of the derivative of concentration with respect to time versus time (dC/dt vs. t) (i.e. the zeroth moment) and then obtaining the first and second moments about the mean.

Evaluation of the tracer breakthrough curve with the method of moments, yielded a mean tracer transit time of 4.29 hours. The corresponding mean tracer velocity as well as the resulting dispersion coefficient and dispersivity are given in Table 5.6.

Table 5.6: Results from Statistical Moment Analysis of TBC (Outflow Port 1)

Mean Travel Time (hrs)	Average velocity (m/s)	Dispersivity (cm)	Dispersion Coefficient (m/s)
4.29	2.59×10^{-5}	0.06	1.60×10^{-6}

The sand tank discharge rate (Port 1): $q = 58 \text{ ml/min} = 9.66 \times 10^{-7} \text{ m}^3/\text{s}$

Cross-sectional area of Sand Tank (Middle chamber): $A = 0.234 \text{ m}^2$

Discharge velocity: $v = \frac{q}{A} = 4.13 \times 10^{-6} \text{ m/s} \dots\dots\dots(5.1)$

Seepage velocity:

$v_s = \frac{v}{n} = \frac{4.13 \times 10^{-6}}{0.32} = 1.29 \times 10^{-5} \text{ m/s} \dots\dots\dots(5.2)$

Where;

n = porosity

The seepage velocity from the Sand Tank model flow characteristics (Eq. 5.2) agrees with the average seepage velocity, computed by the statistical moment analysis of Tracer breakthrough curve (see Table 5.6). The two are within the same order of magnitude.

5.1.5.3 Statistical moments of tracer breakthrough curve for the second discharge rate (160ml/min) through the porous media model.

The first arrival of the chloride tracer was detected at the first observation well (OW_{BM}), 1 hour after tracer injection (see Figure5.7). Six (6) hours after tracer injection, the chloride conductivity reached its maximum of 2.62 mS/cm. After 24 hours, the conductivity had returned to the background value. The sand tank discharge rate (Port 2) stayed at 160ml/min during this time period.

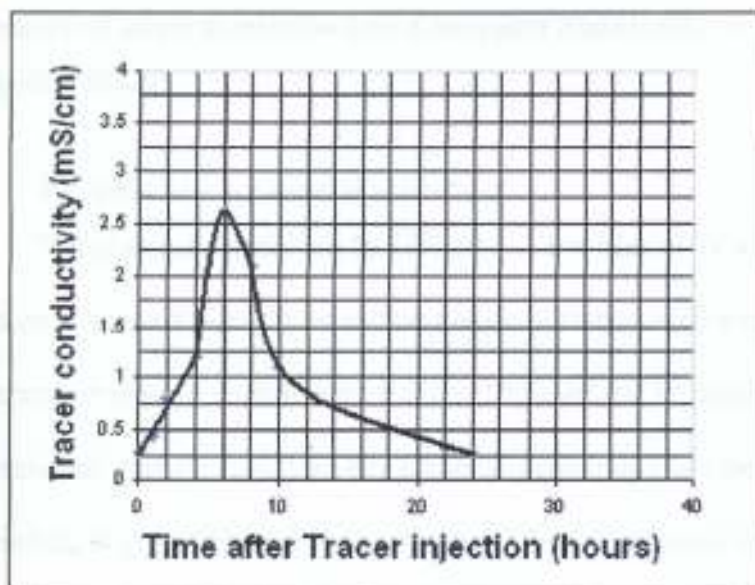


Figure 5.7: Measured Tracer Breakthrough Curve for observation well (OW_{BM}) [Port 2]

Evaluation of the tracer breakthrough curve with the method of moments, yielded a mean tracer transit time of 2.62 hours. The corresponding mean tracer velocity as well as the resulting dispersion coefficient and dispersivity are given in Table 5.7.

Table 5.7: Results from Statistical Moment Analysis of TBC (Outflow Port 2)

Mean Travel Time (hrs)	Average velocity (m/s)	Dispersivity (cm)	Dispersion Coefficient (m/s)
2.62	4.24×10^{-5}	0.1638	6.9×10^{-6}

The sand tank discharge rate (Port 1): $q = 160 \text{ ml/min} = 2.66 \times 10^{-6} \text{ m}^3/\text{s}$

Cross-sectional area of Sand Tank (Middle chamber): $A = 0.234 \text{ m}^2$

$$\text{Discharge velocity: } v = \frac{q}{A} = 1.14 \times 10^{-5} \text{ m/s} \quad \dots\dots\dots(5.3)$$

$$\text{Seepage velocity: } v_s = \frac{v}{n} = \frac{1.14 \times 10^{-5}}{0.32} = 3.55 \times 10^{-5} \text{ m/s} \quad \dots\dots\dots(5.4)$$

The seepage velocity from the Sand Tank model flow characteristics (Equation 5.4) agrees with the average seepage velocity, computed by the statistical moment analysis of tracer breakthrough curve (Table 5.7). The two are within the same order of magnitude.

5.2 Numerical Implementation and Computer Simulation of Tracer Experiments in a Physical Aquifer Model

5.2.1 Physical and numerical modeling

The physical aquifer model (Figure 3.2 and Plate 3.1) was numerically replicated for the simulation of ground water flow and contaminant transport in a tropical porous media soil. Several studies have examined contaminant transport and natural attenuation in porous media soils. Studies have examined data derived from laboratory experiments (Jebellie et al., 2004; Clement et al., 2004; Wildenschild et al., 1994) and field sampling efforts (Hippe and Hall, 1996; Smith and Parrish, 1993; Trevisan et al., 1993;). Results of these studies have shown that numerical modeling technique generally gives useful information on the estimation of solute transport parameters for various soils and the simulation of contaminant fate and transport in porous media. Numerical models, including Hydrocarbon Spill Screening Model (HSSM) (Charbeneau et al., 1995), MT3DMS (Zheng and Wang 1999), RT3D (Clement, 1997), MODFLOW (Harbaugh and McDonald, 1996), BioRedox- MT3DMS (Carey et al., 1999), Bioplume III (Rifai et al., 1997), and Hydrogeosphere (Therrein et al., 2004), have been used in conjunction with field and laboratory data to examine the capabilities of models to simulate contaminant transport and to identify factors affecting attenuation.

5.2.2 Model equations and methods

5.2.2.1 Governing equations

For a homogeneous anisotropic system with coordinate directions aligned with the principal directions of anisotropy, the governing equation for 3D ground water flow is:

$$K_x \frac{\partial^2 h}{\partial x^2} + K_y \frac{\partial^2 h}{\partial y^2} + K_z \frac{\partial^2 h}{\partial z^2} = S_s \frac{\partial h}{\partial t} \tag{5.5}$$

Where K= Hydraulic conductivity , Ss = Storativity, h = Hydraulic head

The advective-dispersive transport equation becomes, in summation form:

$$\frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j} \right) - v_i \frac{\partial c}{\partial x_i} - R \lambda c = R \frac{\partial c}{\partial t} \tag{5.6}$$

$$R = 1 + \frac{\rho_b}{n_e} K_d \quad \dots\dots\dots(5.6a)$$

$$\lambda = (\ln 2) / t_{1/2} \quad \dots\dots\dots(5.6b)$$

Where c = concentration, t = time, v = velocity, x = distance along the direction of flow, D = dispersion coefficient, R = retardation factor, ρ_b = bulk density (soil), n_e = effective porosity (soil) K_d = distribution coefficient, λ = decay constant and $t_{1/2}$ = half-life. The dispersion coefficient is commonly assumed to be proportional to the flow velocity, i.e., $D = \alpha v$, where the proportionality constant α is termed dispersivity.

The partitioning between the solute mass and the sorbed mass is usually expressed by means of a functional relationship, which is a linear reversible partitioning process, under isothermal conditions, and expressed by (Freeze and Cherry, 1979):

$$s = K_d c$$

where K_d is the distribution coefficient.

For $R=1$ and $\lambda=0$ (Advection-Dispersion Model / Non reactive Transport Model). Equation 5.2.2 can be written as;

$$\frac{\partial}{\partial x} \left(D_x \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_y \frac{\partial c}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_z \frac{\partial c}{\partial z} \right) - v_x \frac{\partial c}{\partial x} - \frac{\partial c}{\partial t} = 0 \quad \dots\dots\dots(5.7)$$

5.2.2.2 Boundary and initial conditions

For modeling purposes, the sand tank model was conceptualized as a shallow unconfined aquifer comprised of gravelly sand as porous media material. The specified constant hydraulic heads at the up gradient and down gradient boundaries of the porous medium were 73 and 68.5 cm respectively. Type 2, zero-concentration gradient (Neuman) and Type 3, dispersive flux boundary (Cauchy) contaminant transport boundary conditions were used. Instantaneous contaminant injection was used at an injection rate of 0.7ml/sec for 5 minutes. Background tracer concentration (c_0) was 288mS/cm.

Tracer was injected along the length of the source location (x,y) (110,15). The injection concentration of the tracer was 28.1 mS/cm (12g/l) in line with the injection concentration for the physical aquifer model in the laboratory.

5.2.2.3 Modeling techniques and numerical implementation

Solute transport parameters such as, dispersivity, dispersion coefficients, seepage velocity and effective porosity values of the sand tank were obtained from a tracer transport experiment. The cell-centered finite difference equation was generated for the 3-D flow equation. The 3-D difference equation is:

$$\begin{aligned}
 &K_x \frac{(u_{i-1,j,k} - 2u_{i,j,k} + u_{i+1,j,k})}{\Delta x^2} + K_y \frac{(u_{i,j-1,k} - 2u_{i,j,k} + u_{i,j+1,k})}{\Delta y^2} \\
 &+ K_z \frac{(u_{i,j,k-1} - 2u_{i,j,k} + u_{i,j,k+1})}{\Delta z^2} = S_s \frac{(u_{i,j,k})_t - (u_{i,j,k})}{\Delta t} \tag{5.8}
 \end{aligned}$$

Cell-centered finite difference equivalents for the 3-D Advection-Dispersion equation in equation 6.3 are given as;

$$\begin{aligned}
 &D_x \frac{(c_{i-1,j,k} - 2c_{i,j,k} + c_{i+1,j,k})}{\Delta x^2} + D_y \frac{(c_{i,j-1,k} - 2c_{i,j,k} + c_{i,j+1,k})}{\Delta y^2} \\
 &+ D_z \frac{(c_{i,j,k-1} - 2c_{i,j,k} + c_{i,j,k+1})}{\Delta z^2} = v \frac{(c_{i,j,k})_t - (c_{i,j,k})}{\Delta x} + \frac{(c_{i,j,k})_t - (c_{i,j,k})}{\Delta t} \tag{5.9}
 \end{aligned}$$

We can again write the nodal template form by inspection directly from the difference equation.

Multiplying the difference equation through by the volume $\Delta x \Delta y \Delta z$, and letting

$$a = \frac{D_x \Delta y}{\Delta x}; \quad b = \frac{D_y \Delta x}{\Delta y}; \quad c = \frac{D_z \Delta x \Delta y}{\Delta z}; \quad V = v \Delta x \Delta y \Delta z$$

and $d = 2(a + b + c)$, the finite difference template becomes

$$\begin{aligned}
 &\underbrace{\begin{bmatrix} -a & -b & -c & d & -c & -b & -a \end{bmatrix}}_{M'} + \frac{1}{\Delta x} V \underbrace{\begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}}_{M'} - \frac{1}{\Delta t} \Delta x \Delta y \Delta z \underbrace{\begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}}_{M'} \left\{ \begin{array}{c} c_{i-1,j,k} \\ c_{i,j-1,k} \\ c_{i,j,k-1} \\ c_{i,j,k} \\ c_{i,j,k+1} \\ c_{i,j+1,k} \\ c_{i+1,j,k} \end{array} \right\}_t \\
 &= \frac{1}{\Delta x} V (c_{i,j,k})_{t-\Delta t} + \frac{1}{\Delta t} \Delta x \Delta y \Delta z (c_{i,j,k})_{t-\Delta t} \tag{5.10}
 \end{aligned}$$

The global matrix equation will become;

$$\left\{ [M^D] + [M^V] + \frac{1}{\Delta t} [M^S] \right\} \begin{Bmatrix} c_{i-1,j,k} \\ c_{i,j-1,k} \\ c_{i,j,k-1} \\ c_{i,j,k} \\ c_{i,j,k+1} \\ c_{i,j+1,k} \\ c_{i+1,j,k} \end{Bmatrix} = \frac{\Delta x \Delta y \Delta z}{\Delta t} (c_{i,j,k}) - \Delta t \quad (5.11)$$

Where the individual finite difference matrix templates are:

Dispersion matrix

$$[M^D] = [(-a)(-b)(-c).2(a+b+c)(-c)(-b).(-a)] \quad (5.12)$$

where

$$a = \frac{D_x \Delta y}{\Delta x}; \quad b = \frac{D_y \Delta x}{\Delta y}; \quad c = \frac{D_z \Delta x \Delta y}{\Delta z};$$

Advection matrix (upstream-weighted form)

$$[M^V] = v_x \Delta y [-1..0..0..1..0..0..0] \quad (5.13)$$

Storage matrix

$$[M^S] = \Delta x \Delta y \Delta z [0..0..0..1..0..0..0]$$

This numerical technique entails using an upstream-weighted finite difference scheme for the advection term and an explicit scheme for the dispersion term in the Advection-Dispersion equation (ADE) because these schemes were more stable. The method of finite difference was used to solve the 3-D groundwater flow and the Advection-Dispersion equation, while the FORTRAN computer language was used to code the algorithm and develop the *SandModel* computer code. The results were displayed graphically using the MATLAB application package.

Input parameters used for the '*SandModel*' are based on the calibration of ground water flow and contaminant transport for the physical sand tank model and a review of the pertinent literature.

The experimental aquifer was discretized into 336,000 elements, comprising; 80 layers, 140 rows, and 30 columns ($n_i=140$, $n_j=30$, and $n_k=80$) (Figure 5.8). Details of the co-ordinates for the twelve

observation points are in Table 6.1. Each grid cell was 1.0cm long by 1.0cm wide. The accuracy of a numerical model is partially governed by the grid spacing and time step constraints.

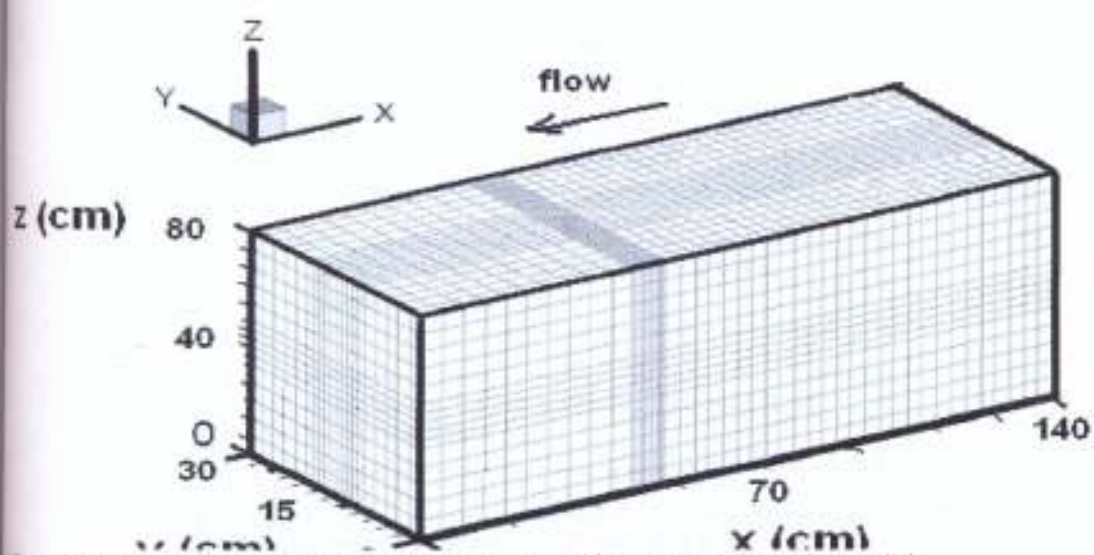


Figure 5.8: Rectangular Finite Difference grids for the Sand Tank Model

Table 5.8: Co-ordinates for Observation Wells in the Sand Tank Model

BT (x,y,z)	BM (x,y,z)	BB (x,y,z)	CT (x,y,z)	CM (x,y,z)	CB (x,y,z)	DT (x,y,z)	DM (x,y,z)	DB (x,y,z)	ET (x,y,z)	EM (x,y,z)	EB (x,y,z)
(70,15,44)	(70,15,24)	(70,15,4)	(70,3,44)	(70,3,24)	(70,3,4)	(70,27,44)	(70,27,24)	(70,27,4)	(30,15,44)	(30,15,24)	(30,15,4)

The grid spacing satisfies the grid Peclet constraints; $P_x = \frac{v_x \Delta x}{D_{xx}} \leq 2$

In the temporal domain, the time step satisfied the Courant criteria given by $C_x = \frac{v_x \Delta t}{\Delta x} \leq 1$

The work on numerical modeling reported here quantitatively explores those patterns and predictions of groundwater and contaminant movement through the sand tank model. The primary tasks involved in developing the groundwater flow and solute transport model are 1) identifying a suitable computer code; 2) selecting the vertical and horizontal extent of the model domain; 3) constructing a finite difference grid for the model domain; 4) overlaying the hydrostratigraphy onto the finite difference grid; 5) assigning boundary conditions to simulate natural hydrogeologic features of the groundwater flow system (Water table, rivers, water divides etc); and 6) specifying hydraulic conductivity and other relevant material properties for each stratigraphic unit or layer. The flow charts

for the main computer program and the two subroutines; Advection and Dispersion are illustrated in Figure 5.9a and Figure 5.9b.

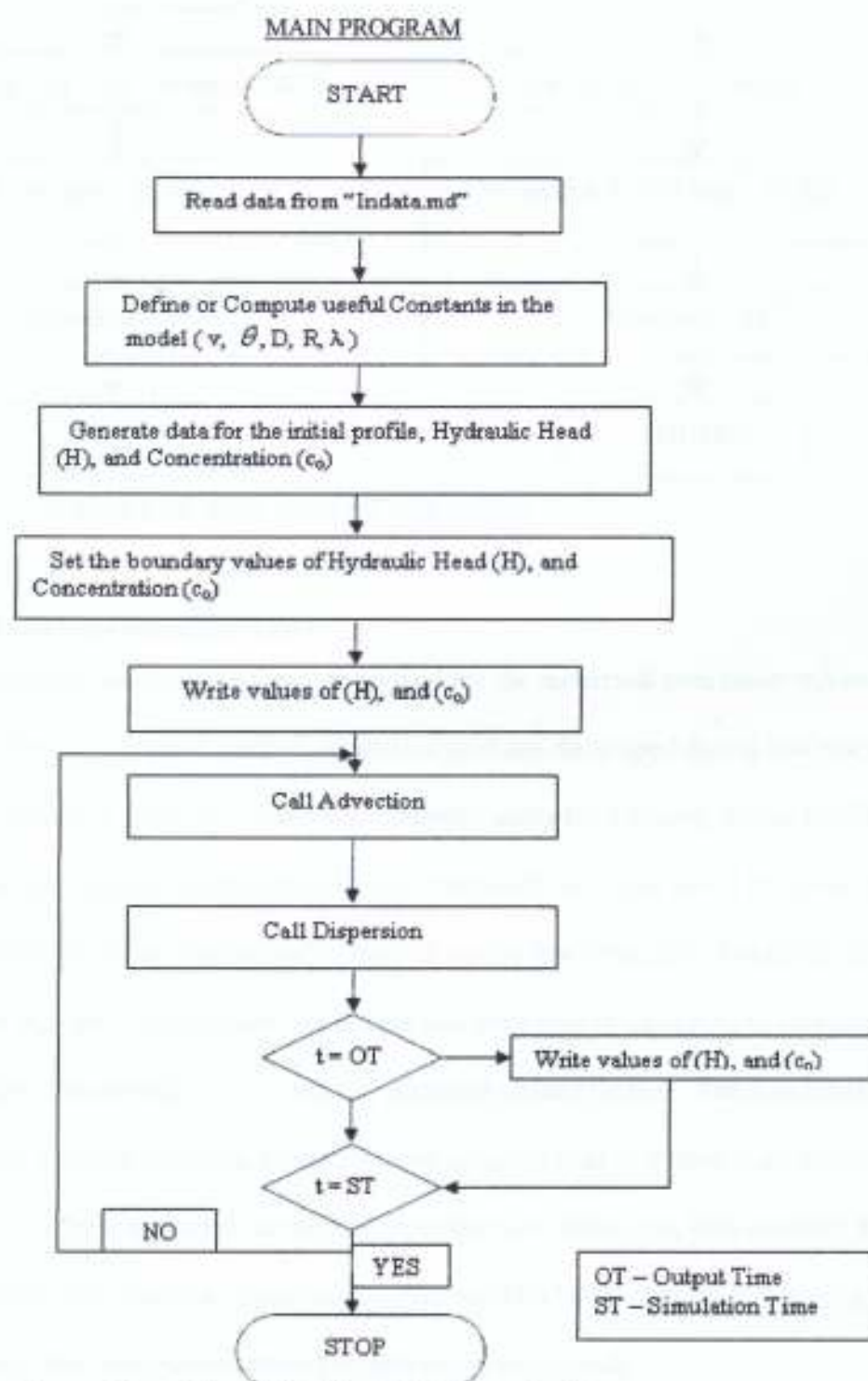
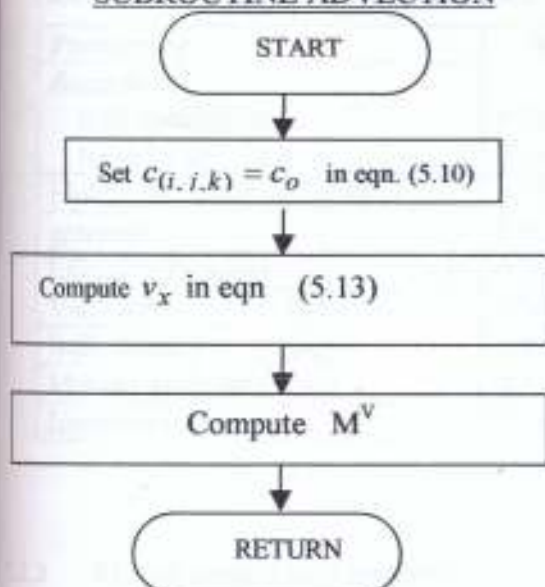


Figure 5.9a: Flow Chart for Main Computer Program

SUBROUTINE ADVECTION



SUBROUTINE DISPERSION

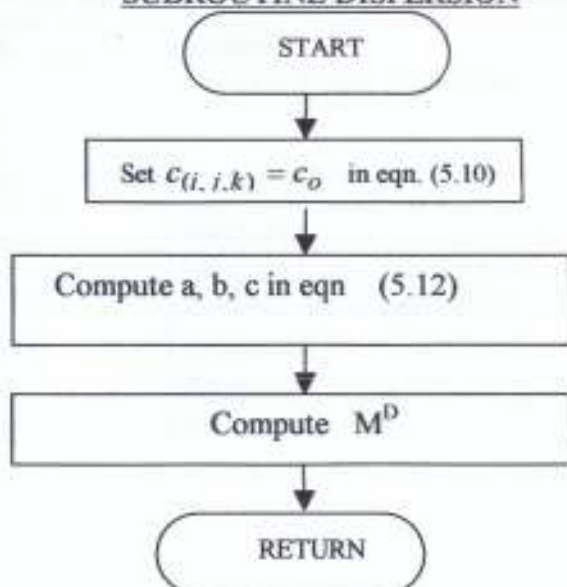


Figure 5.9b: Flow chart for Subroutines

5.2.2.4 *SandModel* computer code

The computer program package developed for the numerical simulation is *SandModel*. It is a groundwater flow and solute transport simulation package developed during this research. The computer was written in FORTRAN and was compiled using the Compaq Visual FORTRAN Compiler. It will run without modification on any Microsoft Windows based PC with sufficient RAM. *SandModel* is a three-dimensional numerical model describing fully-integrated subsurface flow and solute transport. *SandModel* is a unique and ideal tool to simulate the movement of water and solutes within the subsurface in a realistic, physically-based manner. The *SandModel* code was designed so that it can be extended to handle more complex field problems in an efficient and robust manner. It's finite difference numerical approximation technique, fully-coupled analysis and it has compatibility with advanced visualization package MATLAB. For each time step, the model solves subsurface flow and mass transport equations simultaneously.

The model input parameters are presented in Table 5.9

Table 5.9: Flow system parameters used in simulating the laboratory scale tracer experiment

Parameter	Value	Source
dispersivity:		chloride tracer calibration
longitudinal (α_L)	0.06 cm	
transverse (α_T)	0.006cm	
Hydraulic conductivity (K_s)	5.76×10^{-4} m/s	measured
gradient	0.0321	measured
Effective Porosity (n_e)	0.215	chloride tracer calibration
Velocity (v)	2.59×10^{-5} m/s	chloride tracer calibration
Bulk density (ρ_b)	1.9 Mg/m ³	measured
Median grain size (d_{50})	0.55	measured
Injection rate	12 ml/min	measured

5.2.3 Model results and analysis

5.2.3.1 Concentration breakthrough profiles

The numerical model was run in the tracer mode to simulate the observed tracer breakthrough results. Multiple simulations were completed by adjusting the values of the longitudinal and transverse dispersion coefficients, and the value of the effective porosity to fit the breakthrough data collected at all the twelve observation points. A comparison of the measured and simulated breakthrough profiles are shown in Figure 6.3. Statistical comparison of observed and simulated data using the coefficient of determination (R^2), as correlation index and the Paired-t test of significance between sample means at 5% level of significance for the breakthrough curves reveals a high correlation and that there is no significant difference between the observed and simulated data sets. The summary of the statistical analysis for the four observation wells are as follows;

Observation well B [$R^2=0.79$, $N=14$, Calculated $t=-0.579$ with df 13, $P=0.572$ (2-tailed)]

Observation well C [$R^2=0.91$, $N=14$, Calculated $t=0.540$ with df 13, $P=0.598$ (2-tailed)]

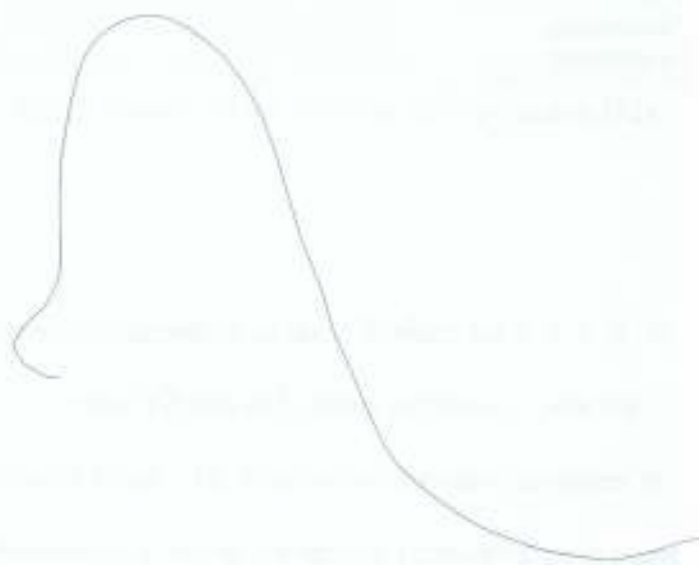
Observation well D [$R^2=0.86$, $N=14$, Calculated $t=1.046$ with df 13, $P=0.315$ (2-tailed)]

Observation well E [$R^2=0.88$, $N=14$, Calculated $t=1.98$ with df 13, $P=0.204$ (2-tailed)]

where; R^2 – Coefficient of Determination
 N – Sample size
 t - t-statistic(student t quantile) [Table 3. Appendix C]
 df – degree of freedom ($N-1$)
 P - calculated probability is the estimated probability of rejecting the **null hypothesis (H_0)** of a study question when that hypothesis is true.

Calculated t value for each well is less than the critical value of t ($t_{\text{critical}} = 2.16$ for $df=13$ [Table 3, Appendix C]), and the calculated P value for each well is greater than the chosen significance level ($P=0.05$), therefore the null (no difference) between observed and simulated data sets hypothesis is accepted. The analysis also reveals high to very high correlation between the observed and simulated values.

Solute transport parameters can be determined by fitting the observed tracer breakthrough response to the Advection-Dispersion transport model for a conservative, nonsorbing solute in a homogeneous porous medium subject to unidirectional flow and three-dimensional dispersion (Chrysikopoulos et al 2000). The calibrated estimates of the model parameter that best fit the profiles are the longitudinal dispersivity value of 0.07, transverse dispersivity value of 0.007, effective porosity value of 0.20 and seepage velocity of 2.2×10^{-5} m/s. These values are in good agreement with those obtained for similar systems by Dela Barre et al., (2002) and Kim et al., (2005).



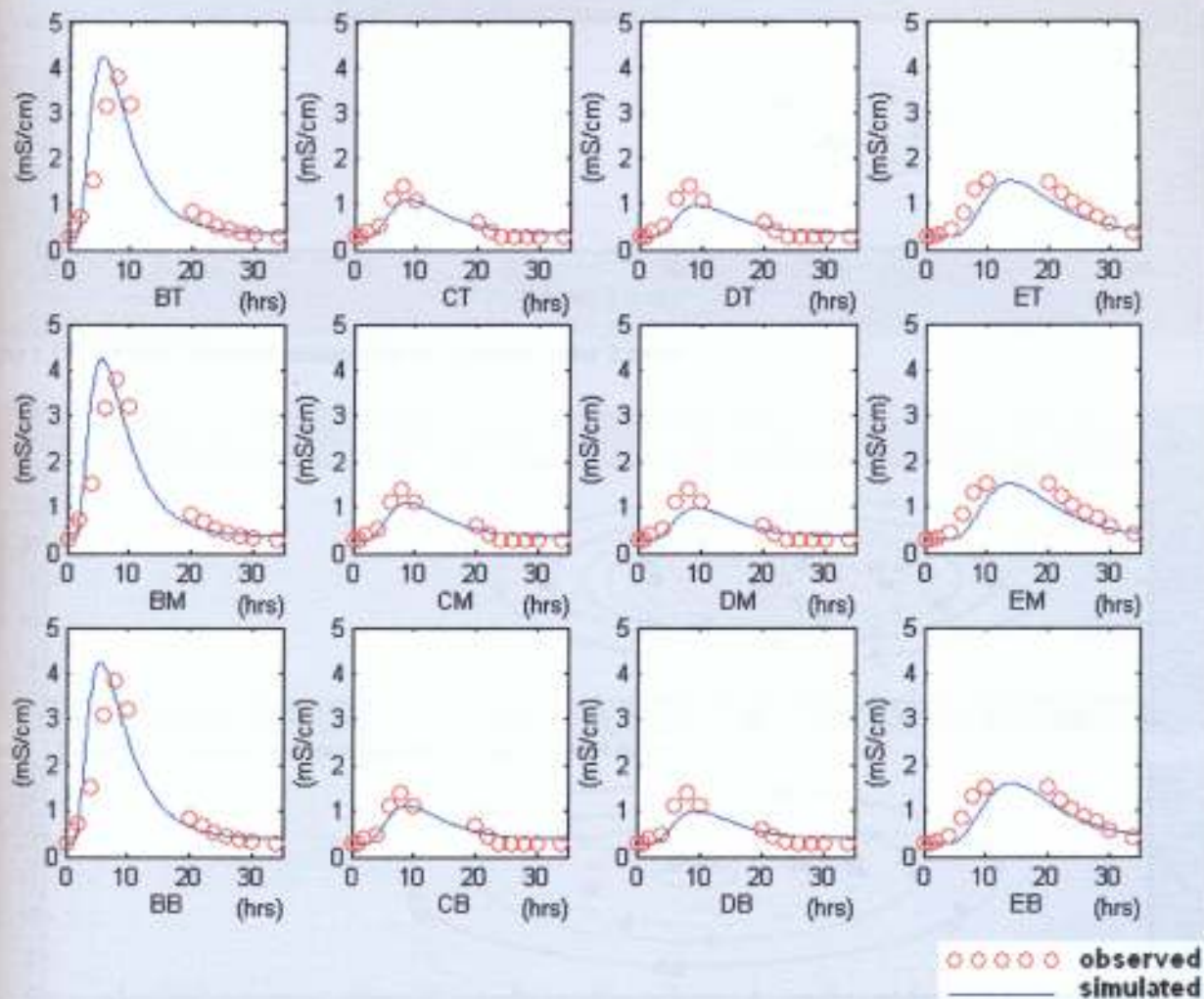


Figure 5.10: Observed and Simulated Chloride Tracer Concentration Profiles for the Twelve (12) Multi-level Observation Points.

5.2.3.2 Spatial plume description

The simulated spread of the injected tracer concentration in the XY-plane for 2, 4, 6, 8, 10, and 30 hours are shown in Figures 5.11 to 5.16. The view YZ and XZ planes in the sand tank for eight (8) hours simulation are presented in Figures 5.17 and 5.18. The isoconcentration contours in Figure 5.14, 5.17 and 5.18 confirms the peak observation of about 3.8 mS/cm concentration at point $B_M(x,y,z) (70,15,24)$ for eight hours of simulation.

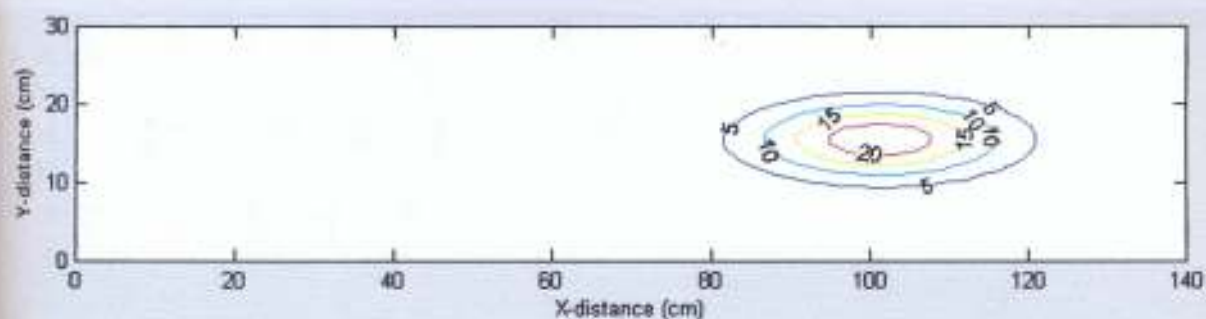


Figure 5.11: XY002 (Tracer Isoconcentration Contours after 2 hours)

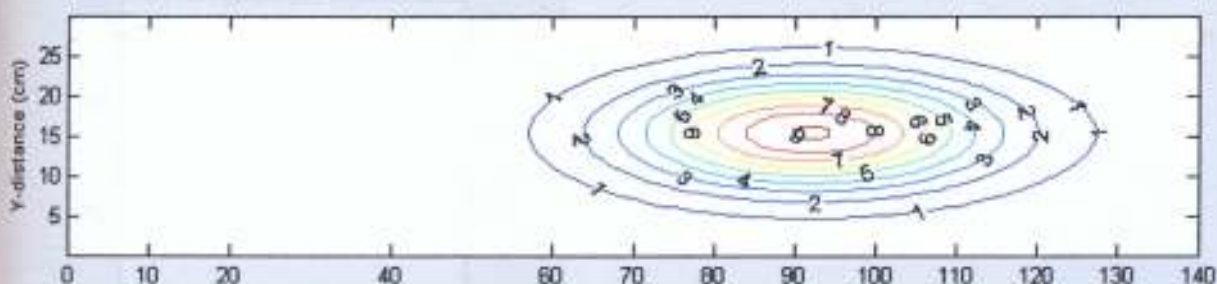


Figure 5.12: XY004 (Tracer Isoconcentration Contours after 4 hours)

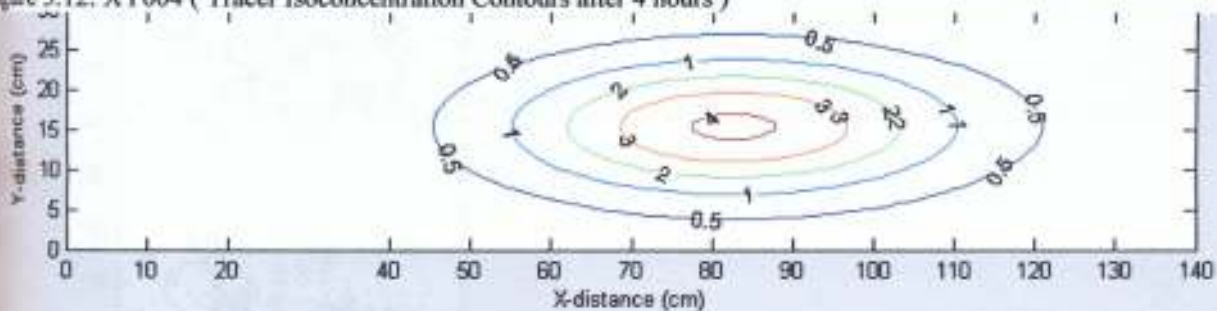


Figure 5.13: XY006 (Tracer Isoconcentration Contours after 6 hours)

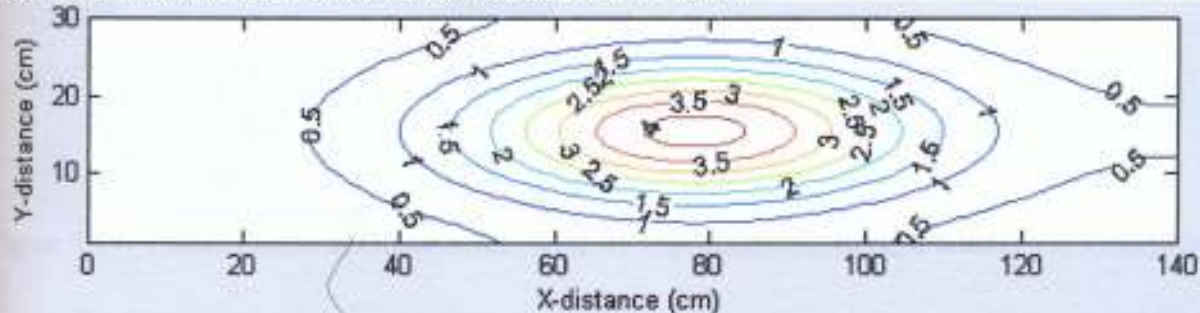


Figure 5.14: XY008 (Tracer Isoconcentration Contours after 8 hours)

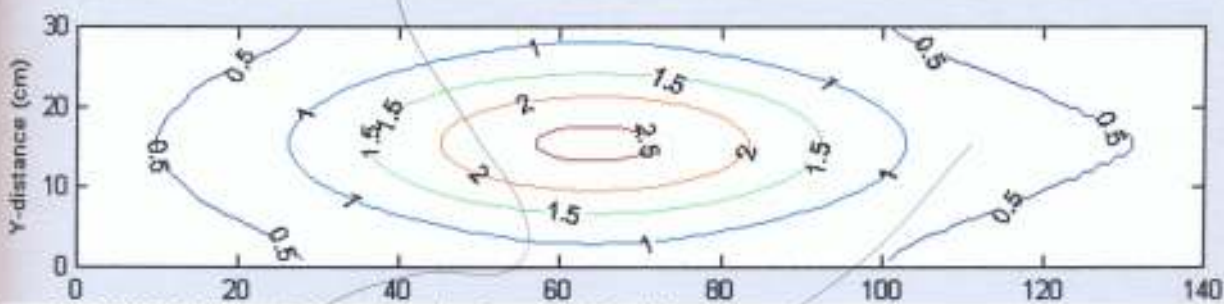


Figure 5.15: XY010 (Tracer Isoconcentration Contours after 10 hours)

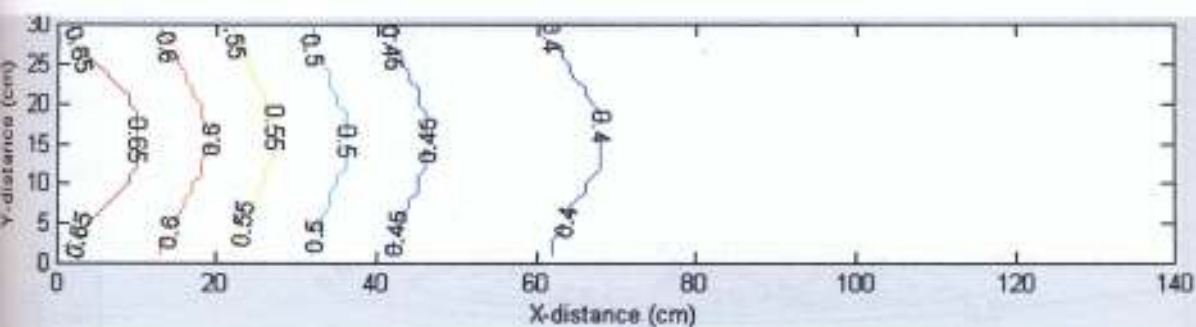


Figure 5.16: XY030 (Tracer Isoconcentration Contours after 30 hours)

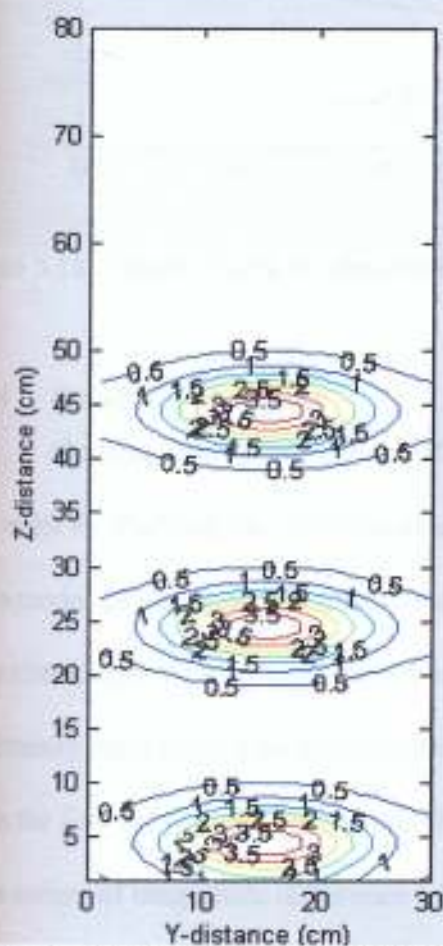


Figure 5.17: Tracer Plume at Observation Well B; Top,Middle,Bottom, 8 hours (YZ View)

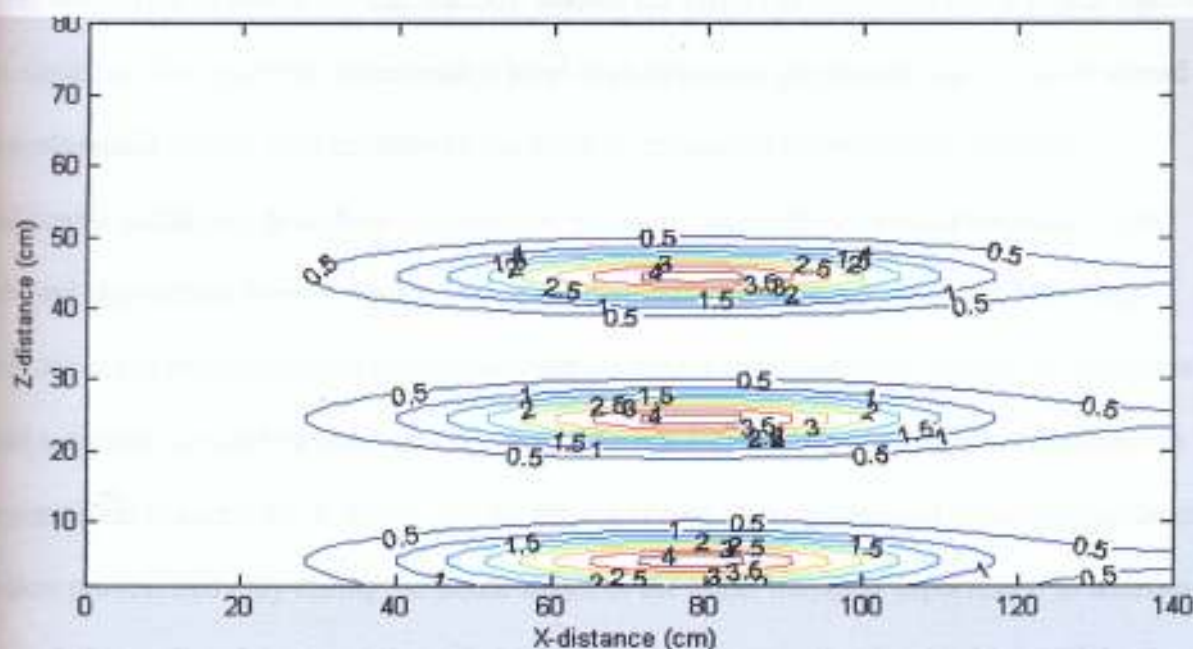


Figure 5.18: Tracer Plume at Observation Well B; Top, Middle, Bottom, 8 hours (XZ View)

5.2.4 Sensitivity Analysis

One can analyze the effects of uncertainties associated with several of the modelled processes by studying the response of the calibrated model to systematic variations in the values of these model parameters. The uncertainty associated with the porous medium properties and bulk flow characteristics were analyzed by varying the hydraulic conductivity and dispersivity. The uncertainty associated with the source definition was analyzed by varying the source concentration.

In the first set of sensitivity simulations, a set of breakthrough profiles were generated using three orders of magnitude difference ($10K$ and $10^{-2}K$) from the measured value of hydraulic conductivity (K). Other model parameters were set at the base level used in the model calibration exercise. Figure 5.19 shows the sensitivity results for the breakthrough curves predicted at OW_{BM} . The figure shows that one order of magnitude increase in the hydraulic conductivity value significantly reduces the concentration levels (42.3%). This is because, when the value of the hydraulic conductivity was increased, the size and connectivity of the porous media material pores increased; this in turn allowed easier flow of the contaminant and reduced residence time.

The second set of sensitivity simulations, studied the effects of variations in the source injection concentration. The injection concentration level is an important parameter that drives the spread of the contaminant. Under field conditions, the value of the source concentration can have considerable variations. In order to evaluate the variations in source concentration values, two additional simulations were completed using the concentration values 10,000 and 14,000mg/l. These two concentrations levels are arbitrary hypothetical values that were selected to access the model sensitivity around the base case scenario. The results for these sensitivity simulations are summarized in Figure 5.20. It shows that the effects of variations in assumed concentration levels are more pronounced only during the initial stages of the tracer transport experiment. In addition as expected, the predicted concentrations are high when the concentration level is high and they are low when the concentration value is low.

Table 5.10: Summary of Sensitivity Analysis

Variable	Value	Max. Plume concentration (mS/cm)	Δ Concentration with Respect to Base Case
Base Case		3.81	
Hydraulic Conductivity K	10K	2.18	- 42.3%
	0.01K	5.50	+ 44.4%
Dispersivity α_L	1000 α_L	3.20	- 16.01%
	1.0 α_L	3.81	0%
Source Concentration C	1.17C	4.78	+ 25.5%
	0.83C	3.24	- 15.0%

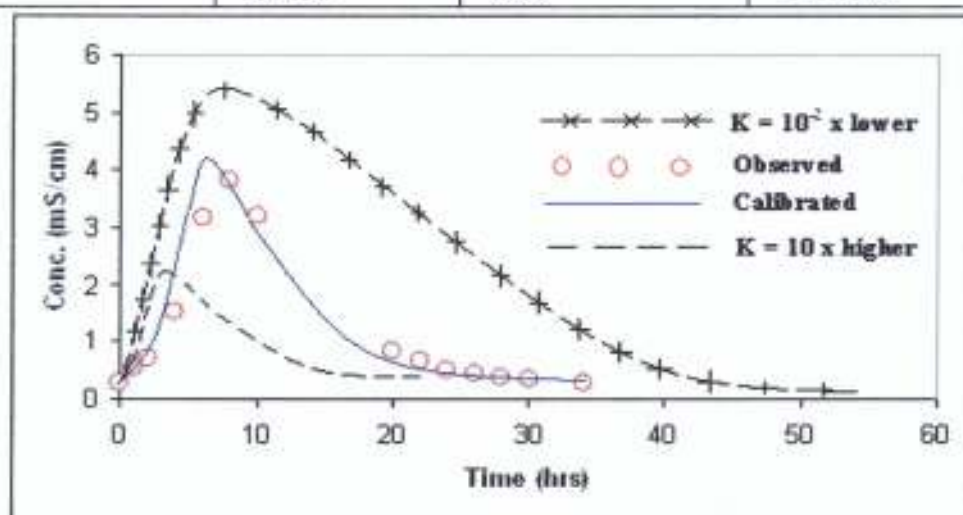


Figure 5.19: Model Sensitivity to Hydraulic Conductivity (Sampling location OW_{BM})

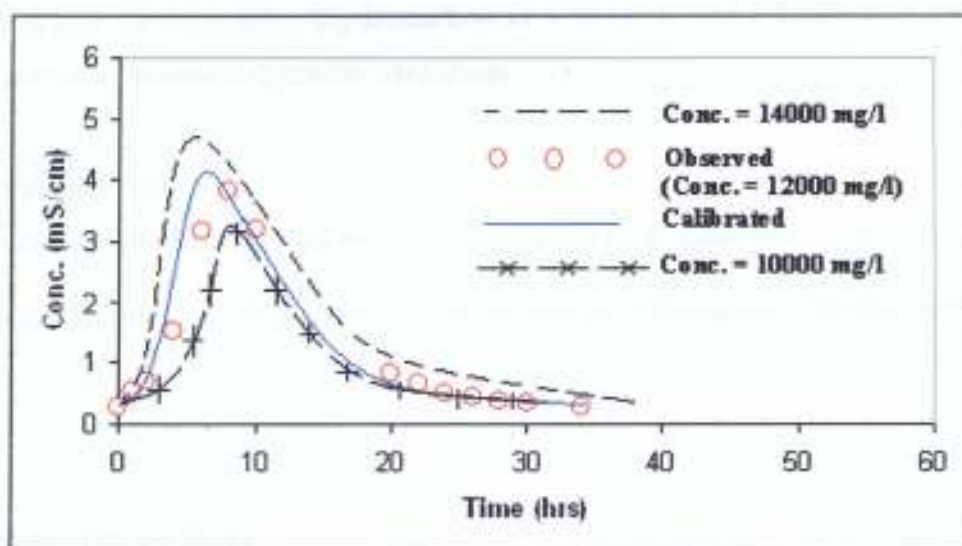


Figure 5.20: Model Sensitivity to Source Concentration (Sampling location OW_{BM})

3 Plume Behaviour for Petroleum Hydrocarbon in a Tropical Sand Tank: Laboratory Experiments and Scenario-Specific Modeling.

3.1 General overview

This study involved the design and implementation of a quasi-natural gradient, laboratory scale aquifer model experiment for the transport of petroleum hydrocarbon (Organic compounds) in groundwater.

3.2 Materials and methods

5.3.2.1 Experimental design

Details of the sand tank experimental set-up including the arrangement of the multilevel sampling pipes are shown in Figure 3.2 and Plate 3.1.

5.3.2.2 Physico-chemical properties

The physico-chemical properties of the gasoline components (BTEX) used in the model are presented in Table 5.11.

Table 5.11: Properties of the gasoline components (BTEX)

Compound	MW ⁽¹⁾ (kg/mole)	Pure Solubility ⁽¹⁾ (kg/m ³)	Phase	Density ⁽²⁾ (kg/m ³)	Diffusion Coefficient ⁽¹⁾ (m ² /s)
Benzene	0.078	1.780		878.6	7.7e-10
Toluene, Ethylbenzene, Xylene	0.104	0.288		870.0	6.2e-10

MW – Molecular Weight

⁽¹⁾ Wiedmeier et al. (1999), Appendix B

⁽²⁾ CRC Handbook of Chemistry and Physics (1980)

5.3.2.3 Analytical procedures

60 ml of unleaded gasoline was injected at the injection well A (Figure 3.2) in the sand tank model using a 20 ml syringe. The flow rate was set at the calibrated 58ml/min value, and hydraulic gradient was 0.0321.

Samples were collected into 40ml glass bottles using a 20ml syringe fitted with siphon tube. The samples were kept below 4°C, using ice packs. Concentration profiles were measured at 1, 8, 15,

and 36 days. The samples were transported to the Multi-Environmental Laboratory Ketu, Lagos for both organic (BTEX) and inorganic analyses.

The parameters analyzed for the groundwater include; Benzene, Toluene, Ethylbenzene, and Xylene (BTEX), light-end components of gasoline, and are of most concern from an environmental impact perspective; Dissolved oxygen (DO), Nitrate (NO_3^-), and Sulphate (SO_4^{2-}), (electron acceptors); Iron II (Fe^{+2}), and Manganese (Mn), bi-products of biological activity.

The BTEX components of gasoline and benzene in particular, are of primary concern because of their relatively high solubility and toxicity at low concentrations.

The gas chromatography apparatus (GC) HP5890, powered with HPCHEM software was used for the BTEX analysis. 10mls of water sample was transferred into the headspace sampler for analysis, using a flame ionization detector (FID). The chromatography was electronically integrated and peak area obtained for a particular BTEX component. A calibration curve was made of concentration against peak area and a response factor obtained for each component.

5.3.3 Results and Analysis

Achieving the goals of this experiment requires analyses of the experimental data base to obtain information about the porous media properties and the movement of the petroleum hydrocarbon (Organic compounds) in time and space. Such information is especially important in quantifying the relative mass loss and apparent retardation of the petroleum hydrocarbon organic solutes, Benzene, Toluene, Ethylbenzene and Xylene (BTEX), and in attempting to validate mathematical models of Advective-dispersive transport.

The results of the BTEX hydrocarbon analyses, for the four periodic sampling sessions are presented in Table 5.12 - 5.15;

Table 5.12: Spatial Distribution of Hydrocarbon concentrations for the 1st sampling session [Day 1]

Groundwater sample ID*	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	Xylene (ppm)	BTEX (ppm)
1AM*	7.94E-01	5.31E-01	5.00E-01	3.98E-01	2.22
1BT	4.56E-03	3.04E-03	2.85E-03	5.01E-03	1.55E-02
1BM	6.13E-03	4.07E-03	3.80E-03	2.76E-03	1.68E-02
1BB	1.97E-03	1.31E-03	1.22E-03	9.37E-04	5.44E-03
1CT	1.77E-03	1.18E-03	1.10E-03	8.58E-04	4.91E-03
1CM	1.64E-03	1.09E-03	1.01E-03	3.66E-04	4.10E-03
1CB	1.39E-03	9.15E-04	8.44E-04	6.74E-04	3.82E-03
1DT	1.79E-03	6.60E-04	1.10E-03	8.54E-04	4.41E-03
1DM	1.12E-03	7.34E-04	6.75E-04	4.00E-04	2.92E-03
1DB	1.13E-03	7.45E-04	6.91E-04	5.15E-04	3.08E-03
1ET	1.27E-03	8.39E-04	7.81E-04	5.88E-04	3.48E-03
1EM	9.22E-04	6.09E-04	5.68E-04	4.83E-04	2.58E-03
1EB	1.61E-03	1.08E-03	1.03E-03	8.40E-04	4.55E-04
Control*	6.91E-09	2.33E-09	2.93E-08	2.59E-07	2.97E-07
Pure Phase Hydrocarbon (Petrol)	7.81	5.24	4.99	3.81	21.86

*Sample ID – Sample Identification

*1AM – 1st sampling session, location A(Middle): Figure 3.2

[Co-ordinates (x,y,z) = (110,15,24)] :

*Control groundwater samples are the water sample collected from the flowing laboratory aquifer model before contaminant (Petroleum Hydrocarbon) injection.

Table 5.13: Spatial Distribution of Hydrocarbon concentrations for the 2nd sampling session [Day 8]

Groundwater Sample ID	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	Xylene (ppm)	BTEX (ppm)
2AM	7.42E-02	4.91E-02	4.63E-02	3.79E-02	2.08E-01
2BT	3.97E-03	2.64E-03	2.48E-03	1.88E-03	1.10E-02
2BM	4.33E-03	2.87E-03	2.68E-03	1.95E-03	1.18E-02
2BB	1.83E-03	1.21E-03	1.13E-03	8.69E-04	5.04E-03
2CT	1.17E-03	7.62E-04	7.24E-04	2.57E-04	2.91E-03
2CM	1.39E-03	9.16E-04	8.50E-04	6.89E-04	3.85E-03
2CB	1.25E-03	8.24E-04	7.60E-04	6.07E-04	3.44E-03
2DT	1.79E-03	6.61E-04	1.10E-03	8.54E-04	4.41E-03
2DM	1.07E-03	7.04E-04	6.48E-04	3.84E-04	2.81E-03
2DB	9.94E-04	6.57E-04	6.09E-04	4.55E-04	2.72E-03
2ET	1.24E-03	8.20E-04	7.69E-04	6.29E-04	3.46E-03
2EM	9.17E-04	5.99E-04	5.66E-04	5.04E-04	2.58E-03
2EB	7.70E-04	5.02E-04	4.72E-03	3.61E-04	2.11E-03
Control	6.91E-09	2.33E-09	2.93E-08	2.59E-07	2.97E-07

Table 5.14: Spatial Distribution of Hydrocarbon concentrations for the 3rd sampling session [Day 15]

Groundwater Sample ID	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	Xylene (ppm)	BTEX (ppm)
3AM	8.84E-05	2.11E-05	1.29E-05	8.42E-05	2.07E-04
3BT	7.38E-05	1.75E-05	1.05E-05	7.09E-05	1.73E-04
3BM	8.38E-05	2.00E-05	1.21E-05	9.40E-05	2.10E-04
3BB	8.23E-05	2.10E-05	1.20E-05	7.65E-05	1.92E-04
3CT	7.22E-05	1.47E-05	1.09E-05	6.82E-05	1.01E-04
3CM	7.22E-05	1.47E-05	1.09E-05	6.82E-05	1.01E-04
3CB	7.22E-05	1.47E-05	1.09E-05	6.82E-05	1.01E-04
3DT	5.96E-05	1.77E-05	1.52E-04	8.11E-04	1.74E-04
3DM	5.96E-05	1.77E-05	1.52E-04	8.11E-04	1.74E-04
3DB	5.96E-05	1.77E-05	1.52E-04	8.11E-04	1.74E-04
3ET	7.05E-05	1.53E-05	9.86E-06	6.42E-05	1.60E-04
3EM	5.04E-05	1.13E-05	8.32E-06	5.23E-05	1.22E-04
3EB	6.97E-05	2.21E-05	1.24E-05	6.22E-05	1.57E-04
Control	6.91E-09	2.33E-09	2.93E-08	2.59E-07	2.97E-07

Table 5.15: Spatial Distribution of Hydrocarbon concentrations for the 4th sampling session [Day 36]

Groundwater Sample ID	Benzene (ppm)	Toluene (ppm)	Ethylbenzene (ppm)	Xylene (ppm)	BTEX (ppm)
4AM	4.43E-06	1.05E-06	6.32E-07	4.25E-06	1.04E-05
4BM	4.83E-06	1.20E-06	6.53E-07	4.34E-06	1.10E-05
4EM	4.33E-06	8.84E-07	6.54E-07	4.09E-06	9.07E-04
Control	6.91E-09	2.33E-09	2.93E-08	2.59E-07	2.97E-07

The graphs for BTEX concentration breakthrough profiles for water samples are presented Figures 5.21 - 5.32. Figures 5.33 and 5.34 are the plots for the soil BTEX concentrations. Near source observation well OW_B, OW_C and OW_D present higher peak concentrations than the down gradient well OW_E. There is no significant difference in the BTEX concentrations at different levels, within the same sampling location. This is probably due to the homogeneity of the porous medium material. Within thirty six (36) days of continuous flow in the sand tank model, the BTEX concentration had reduced to a value close to the background concentration.

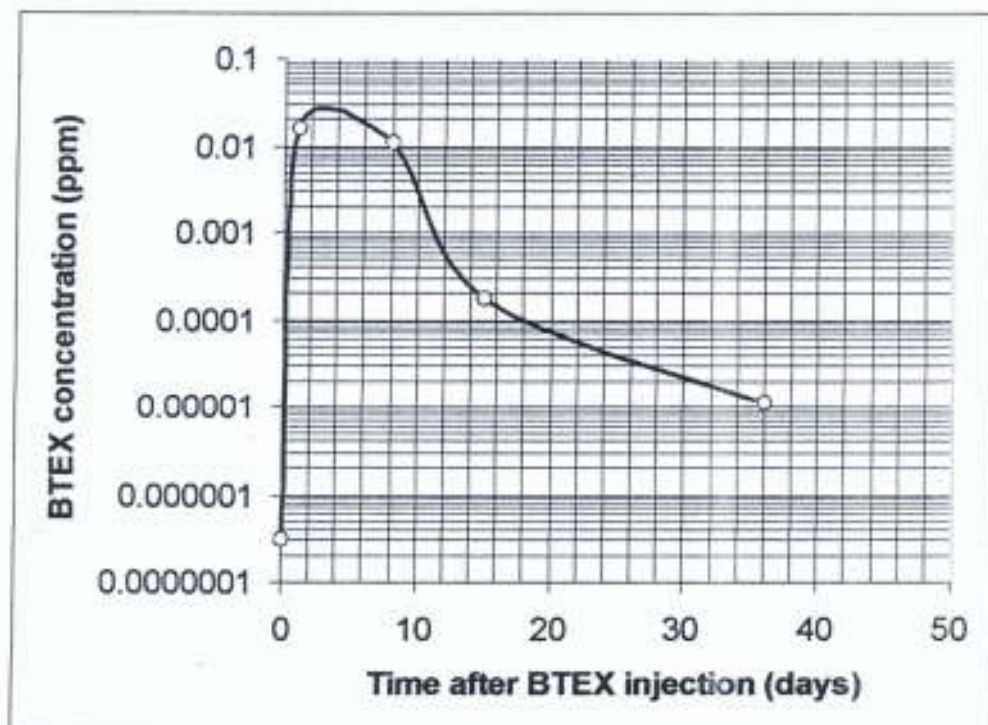


Figure 5.21: Measured BTEX Breakthrough Curve for observation well (OW_{BT})

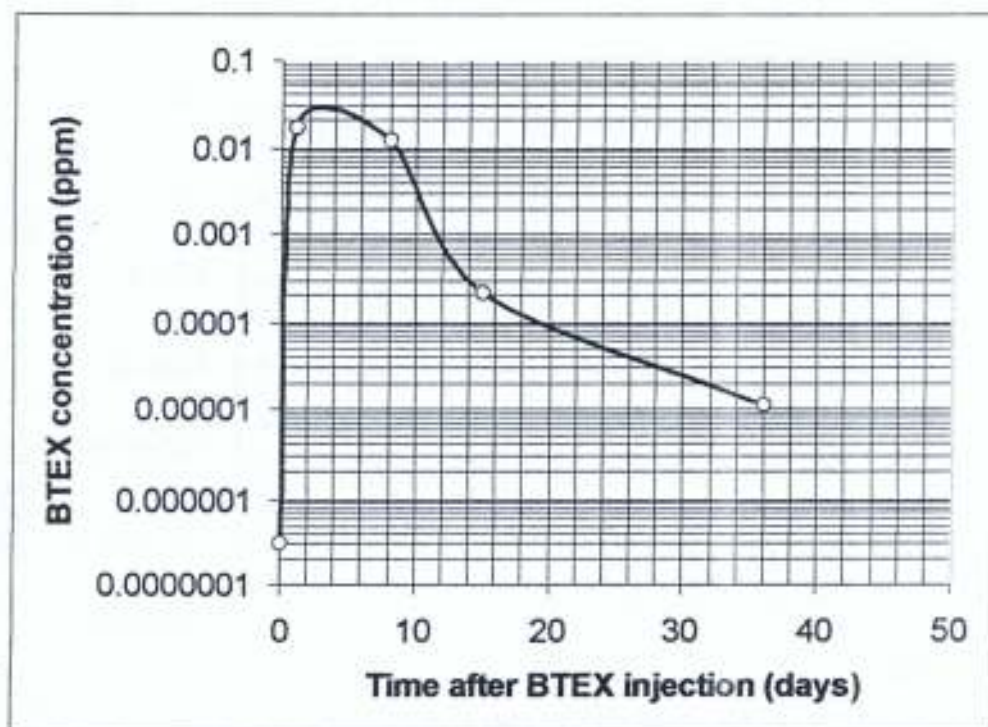


Figure 5.22: Measured BTEX Breakthrough Curve for observation well (OW_{BM})

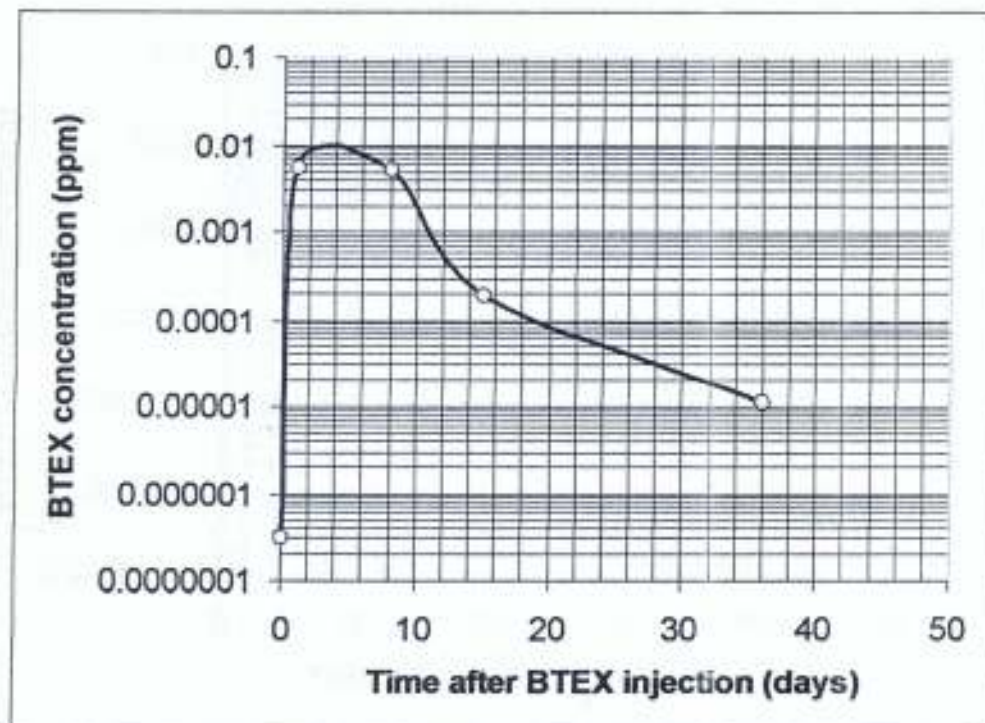


Figure 5.23: Measured BTEX Breakthrough Curve for observation well (OW_{BB})

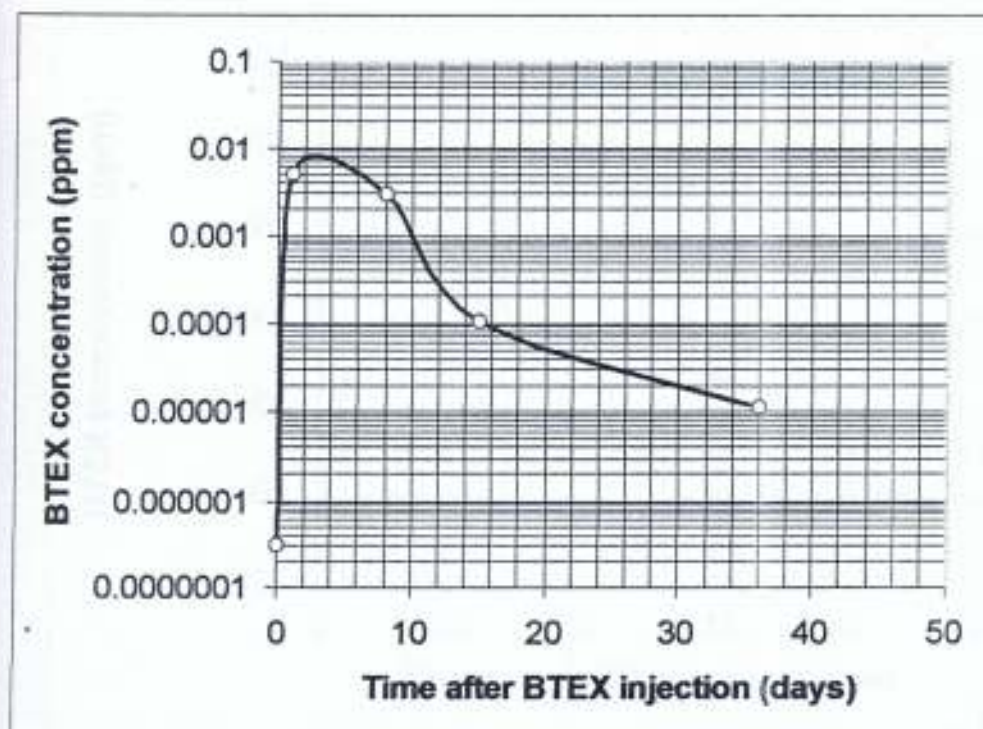


Figure 5.24: Measured BTEX Breakthrough Curve for observation well (OW_{CT})

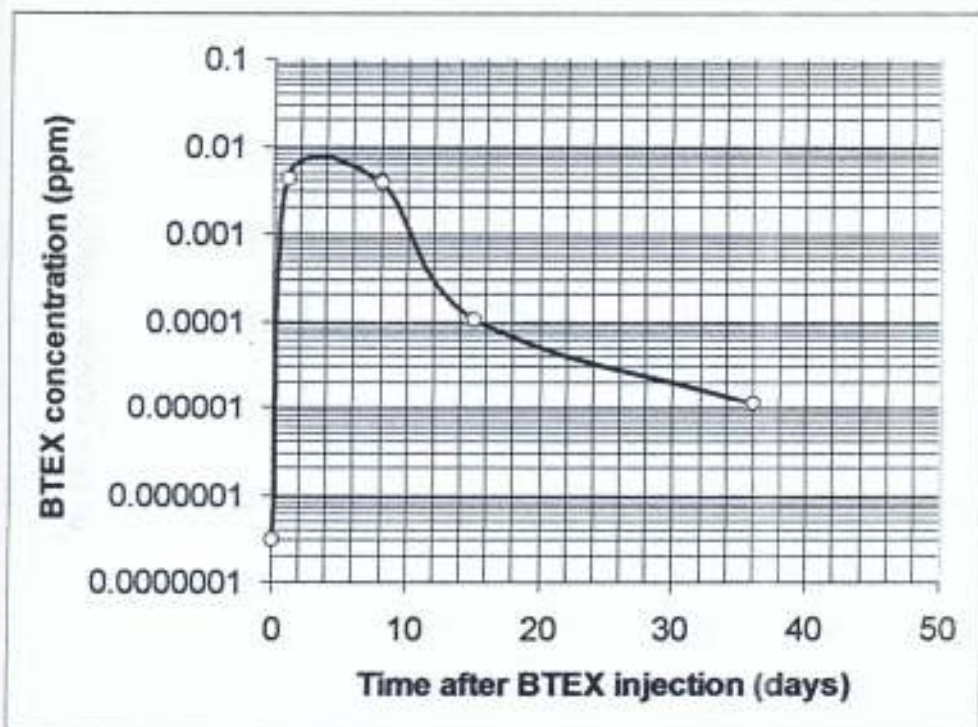


Figure 5.25: Measured BTEX Breakthrough Curve for observation well (OW_{CM})

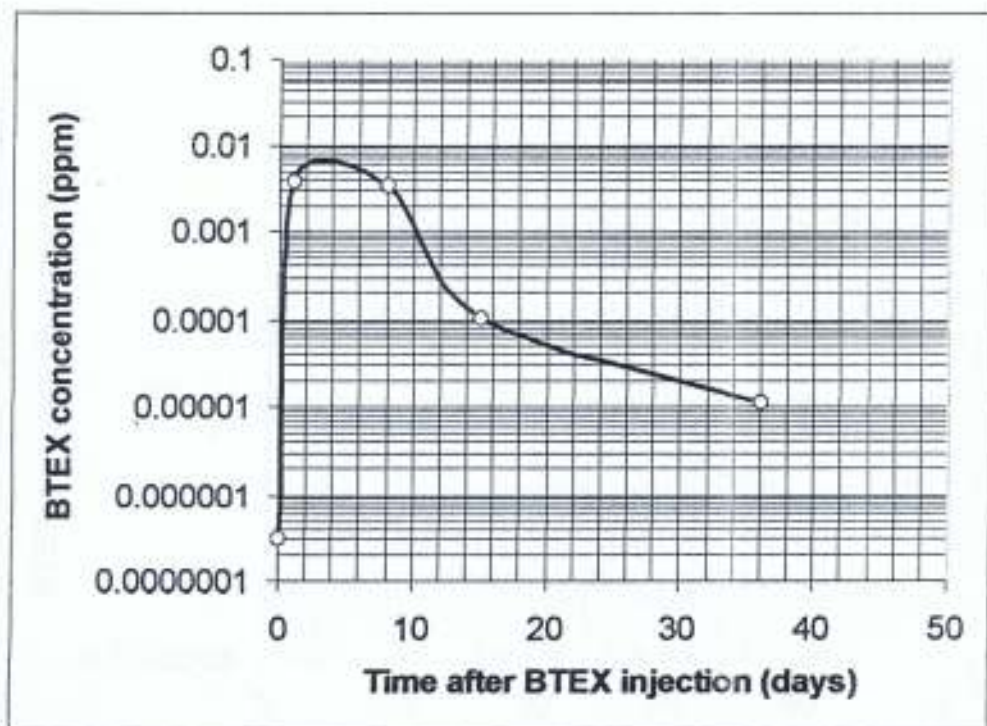


Figure 5.26: Measured BTEX Breakthrough Curve for observation well (OW_{CB})

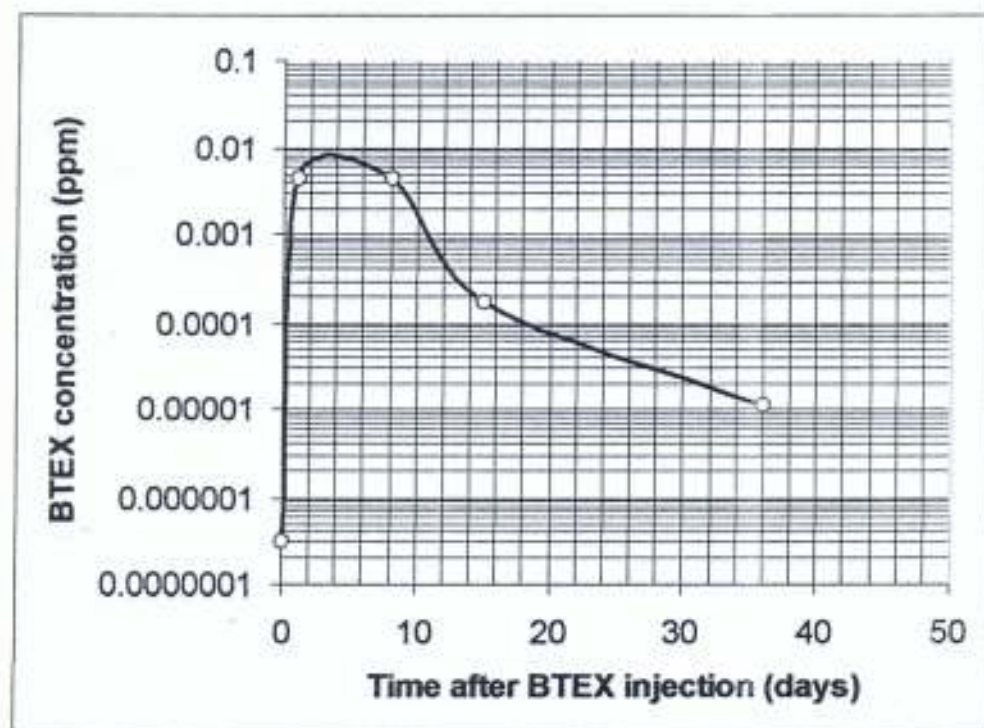


Figure 5.27: Measured BTEX Breakthrough Curve for observation well (OW_{DT})

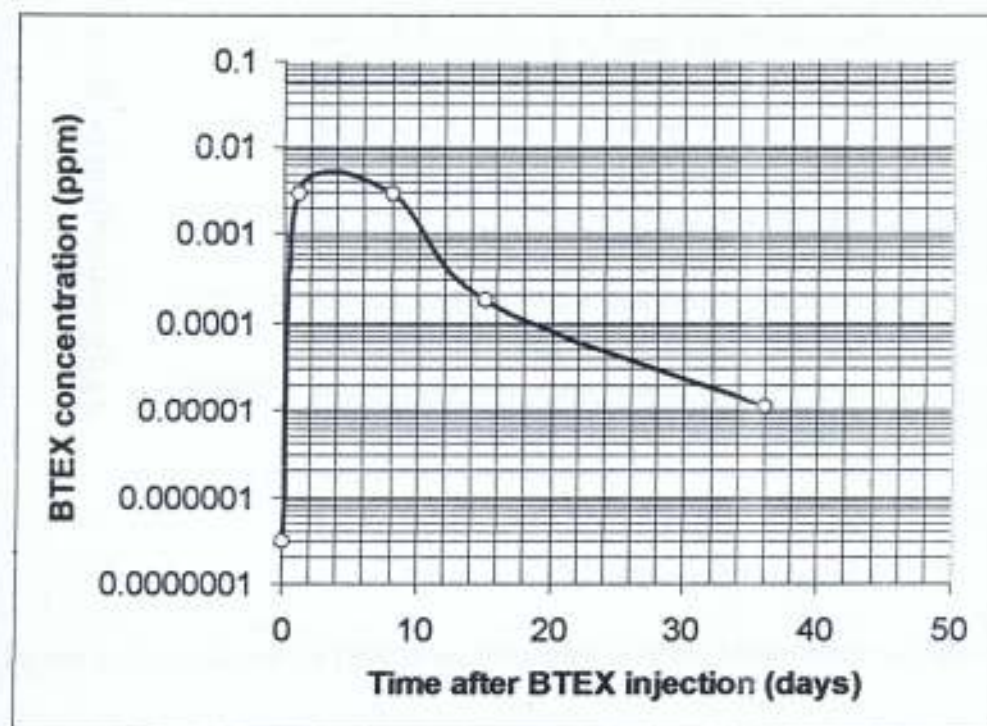


Figure 5.28: Measured BTEX Breakthrough Curve for observation well (OW_{DM})

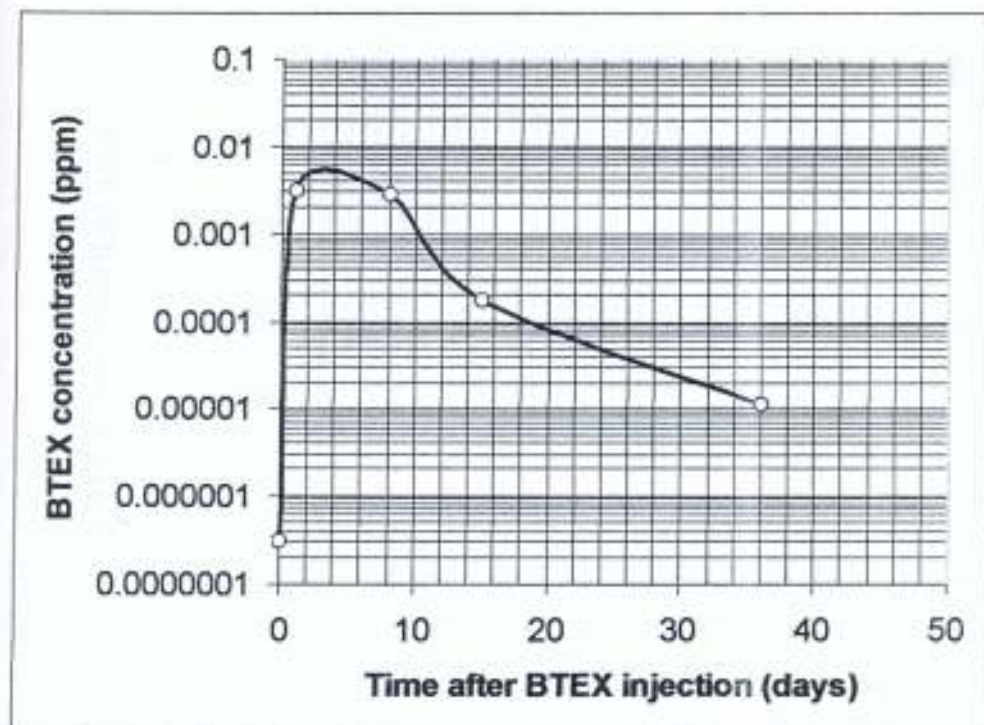


Figure 5.29: Measured BTEX Breakthrough Curve for observation well (OW_{DB})

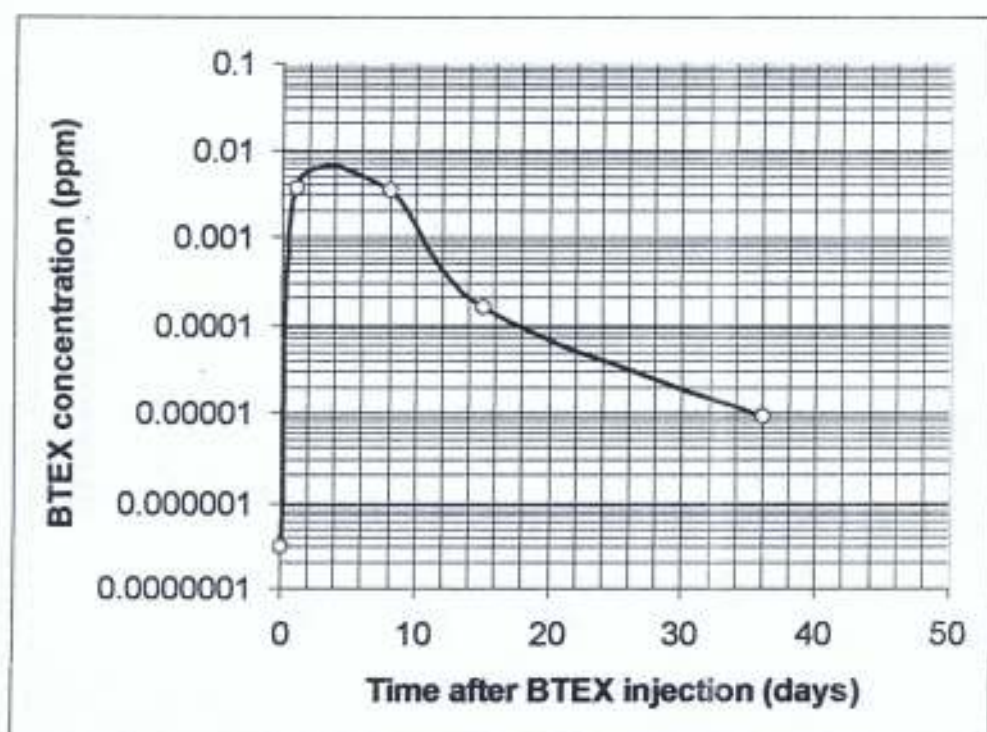


Figure 5.30: Measured BTEX Breakthrough Curve for observation well (OW_{ET})

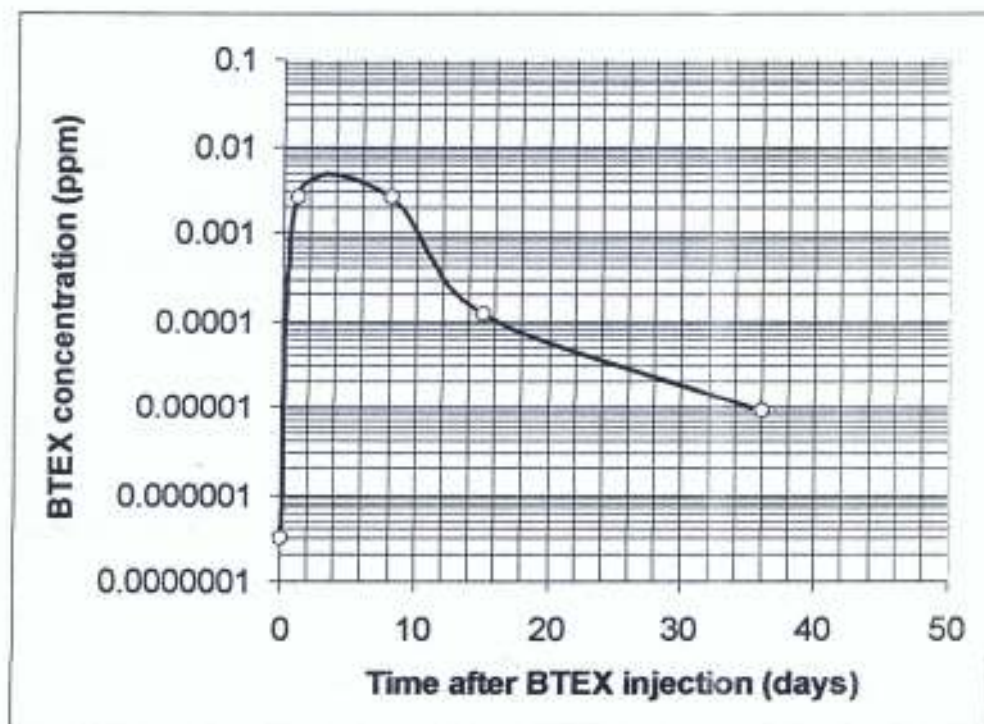


Figure 5.31: Measured BTEX Breakthrough Curve for observation well (OW_{EM})

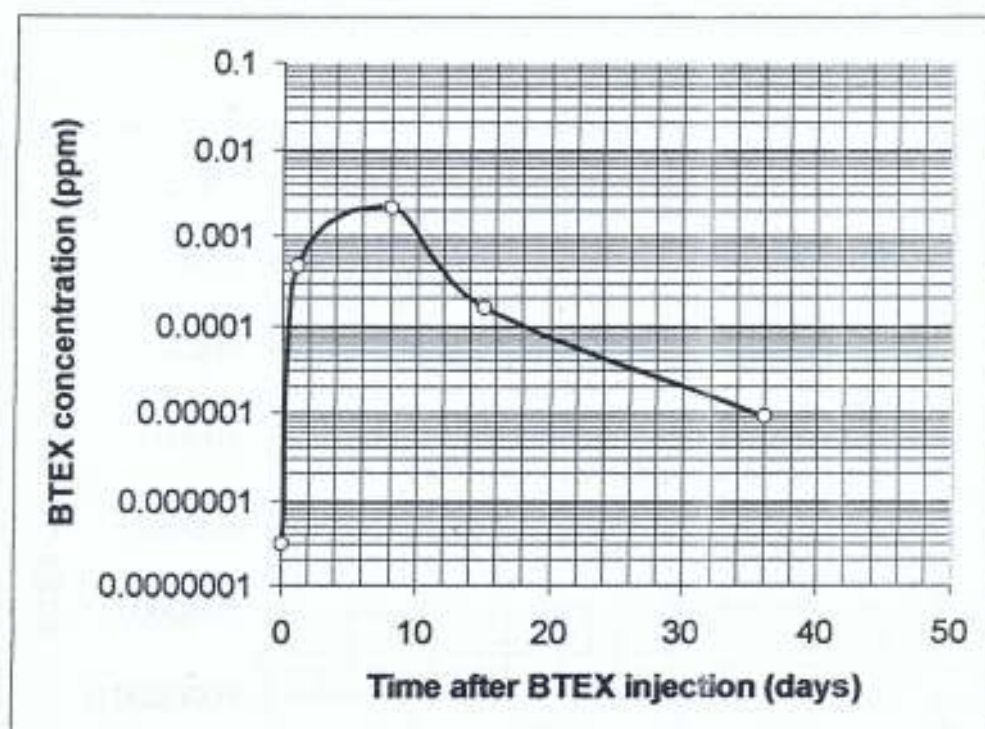


Figure 5.32: Measured BTEX Breakthrough Curve for observation well (OW_{EB})

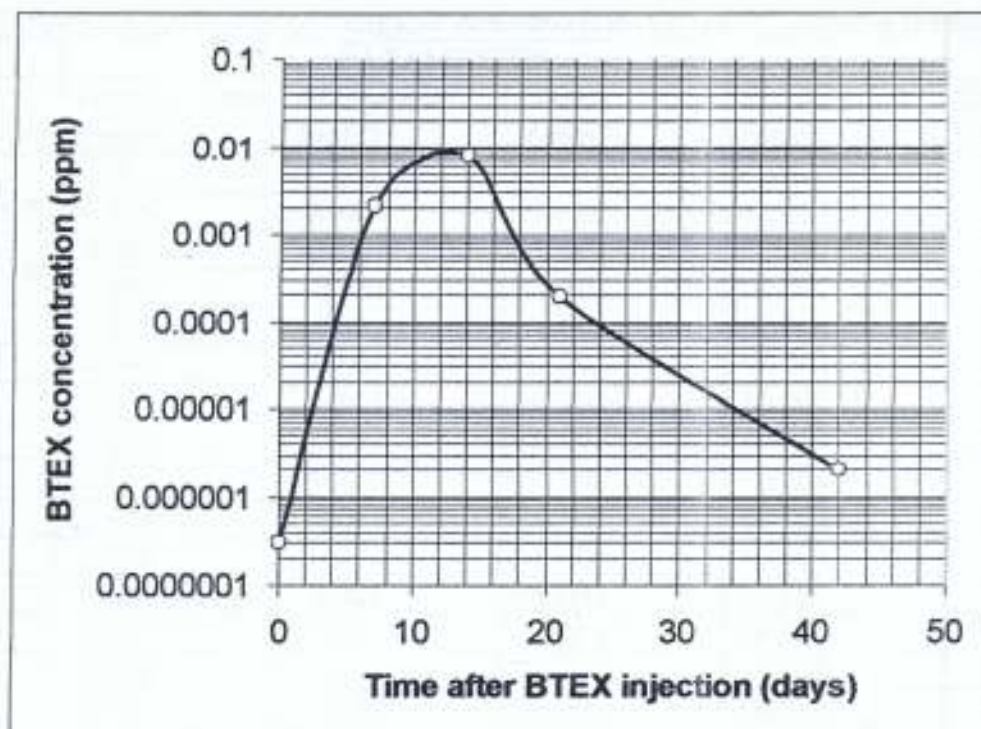


Figure 5.33: Measured BTEX Breakthrough Curve for Soil around (OW_{BM})

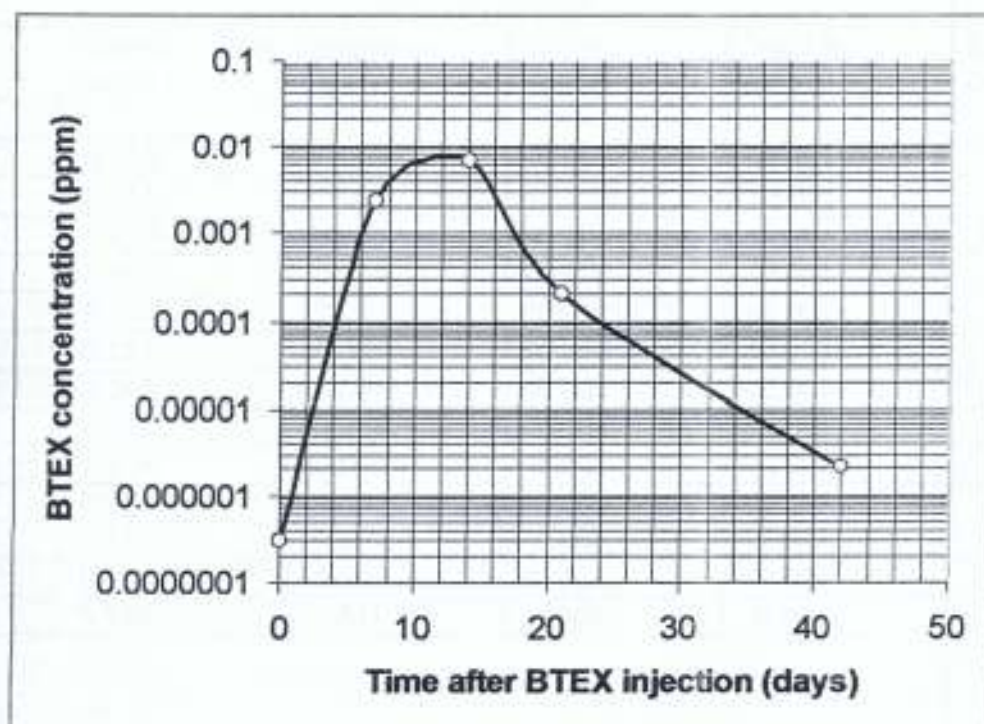


Figure 5.34: Measured BTEX Breakthrough Curve for Soil around (OW_{EM})

The results for the inorganic chemical analyses of the ground water samples are presented in Tables 5.16 – 5.19.

Table 5.16: Spatial Distribution of Inorganic concentrations for the 1st sampling session [Day 1]

Sample ID	PARAMETERS				
	Ferrous iron (ppm)	Manganese (ppm)	Nitrate (ppm)	Sulphate (ppm)	Dissolved Oxygen (ppm)
CONTROL*	0.028	<0.001	<0.001	<0.001	16.56
A(M)	0.085	<0.001	<0.001	<0.001	5.34
B(T)	0.095	<0.001	<0.001	<0.001	2.35
B(M)	0.098	0.001	<0.001	<0.001	4.33
B(B)	0.095	0.001	<0.001	<0.001	2.52
C(T)	0.096	0.001	<0.001	<0.001	1.50
C(M)	0.094	0.001	<0.001	<0.001	2.10
C(B)	0.098	0.001	<0.001	<0.001	1.82
D(T)	0.095	0.001	<0.001	<0.001	1.20
D(M)	0.123	0.001	<0.001	<0.001	1.00
D(B)	0.095	0.001	<0.001	<0.001	2.00
E(T)	0.047	0.001	<0.001	<0.001	1.20
E(M)	0.032	0.001	<0.001	<0.001	1.25
E(B)	0.034	<0.001	<0.001	<0.001	1.20

CONTROL groundwater samples are the water sample collected from the flowing laboratory aquifer model before contaminant (Petroleum Hydrocarbon) injection.

Table 5.17: Spatial Distribution of Inorganic concentrations for the 2nd sampling session [Day 8]

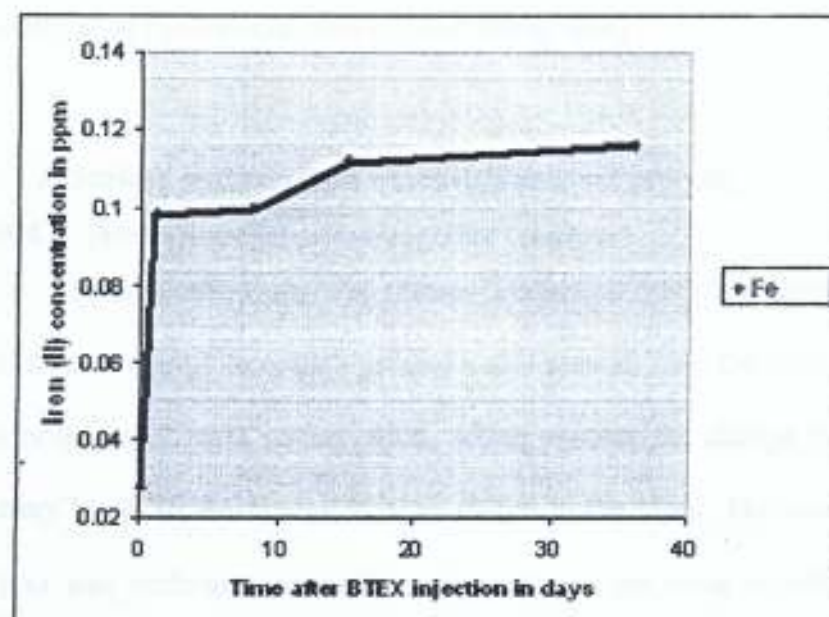
Sample ID	PARAMETERS				
	Ferrous iron (ppm)	Manganese (ppm)	Nitrate (ppm)	Sulphate (ppm)	Dissolved Oxygen (ppm)
A(M)	0.116	0.001	<0.001	0.001	1.80
B(T)	0.111	0.001	<0.001	<0.001	1.85
B(M)	0.100	0.001	<0.001	<0.001	1.82
B(B)	0.099	0.001	<0.001	0.001	1.63
C(T)	0.114	0.001	<0.001	<0.001	1.45
C(M)	0.124	0.001	<0.001	<0.001	1.44
C(B)	0.101	<0.001	<0.001	<0.001	1.20
D(T)	0.111	0.001	<0.001	<0.001	1.25
D(M)	0.108	0.001	<0.001	<0.001	1.22
D(B)	0.084	<0.001	<0.001	<0.001	1.24
E(T)	0.127	0.001	<0.001	<0.001	1.36
E(M)	0.125	<0.001	<0.001	<0.001	1.25
E(B)	0.132	0.001	0.001	0.001	0.50

Table 5.18: Spatial Distribution of Inorganic concentrations for the 3rd sampling session [Day 15]

Sample ID	PARAMETERS				
	Ferrous iron (ppm)	Manganese (ppm)	Nitrate (ppm)	Sulphate (ppm)	Dissolved Oxygen (ppm)
A(M)	0.142	0.001	<0.001	0.001	1.02
B(T)	0.134	0.001	<0.001	<0.001	1.66
B(M)	0.112	0.001	<0.001	<0.001	1.57
B(B)	0.102	0.001	<0.001	0.001	1.36
C(M)	0.128	0.001	<0.001	<0.001	1.33
D(M)	0.116	0.001	<0.001	<0.001	1.19
E(T)	0.114	0.002	<0.001	<0.001	1.32
E(M)	0.111	0.002	<0.001	<0.001	1.09
E(B)	0.121	0.002	<0.001	0.001	0.85

Table 5.19: Spatial Distribution of Inorganic concentrations for the 4th sampling session [Day 36]

Sample ID	PARAMETERS				
	Ferrous iron (ppm)	Manganese (ppm)	Nitrate (ppm)	Sulphate (ppm)	Dissolved Oxygen (ppm)
A(M)	0.199	0.003	<0.001	0.001	0.66
B(M)	0.116	0.003	<0.001	<0.001	0.82
E(M)	0.148	0.003	<0.001	<0.001	0.74

Figure 5.35: Measured iron (II) concentration for observation well (OW_{BM})

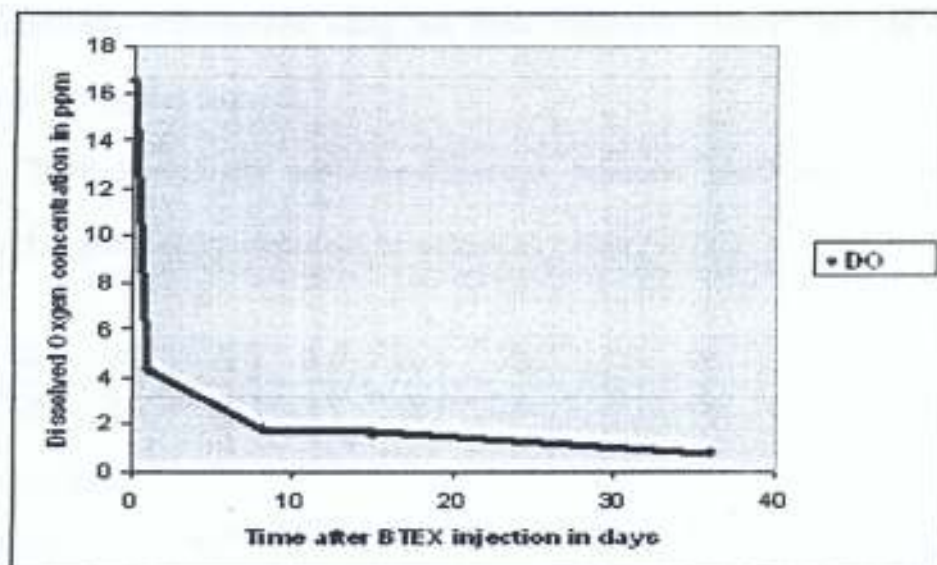


Figure 5.36: Measured dissolved oxygen concentration for observation well (OW_{BM})

The graphs for Iron (II) and dissolved concentrations for water samples at observation well (OW_{BM}) are presented in Figures 5.35 and 5.36. The other inorganic parameters have not shown a significant trend. These geochemical parameters show a pattern indicating natural attenuation (Barker and Mayfield 1988; Metzinger and Capps 1997). During the high contamination period, the observation well had depleted electron acceptors (dissolved oxygen and nitrate) and a high concentration of byproducts (iron (II) and manganese).

5.3.4 Modeling hydrocarbon reactive transport process

5.3.4.1 Advective-dispersive/reactive transport

The advective-dispersive transport equation describes the transport of a solute (a miscible contaminant or tracer) through a ground water system. Like the fluid continuity equation, it is based on the principle of mass conservation, which equates the change in the mass passing through an elementary block to the change in mass stored in the block. However, since solutes in general can also react and undergo chemical transformations, we must include terms allowing for reactive changes. Sorption of a contaminant onto aquifer solids results in retardation effects, whereas decay (e.g. from radioactive wastes) decreases the mass.

Concentration profiles were measured at 1, 8, 15, and 36 days and modelled using the solution to the Advective-Dispersive Equation (ADE), incorporation sorption and decay components. This

was numerically implemented using the finite difference method and the *SandModel* software developed during this research.

The Three-dimensional advective-dispersive equation (mathematical model), incorporating sorption and decay components can be written as { Bear (1972)};

$$\frac{\partial}{\partial x}\left(D_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_y \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_z \frac{\partial c}{\partial z}\right) - v_x \frac{\partial c}{\partial x} - R\lambda c - R \frac{\partial c}{\partial t} = 0 \quad (5.14)$$

or in vector form:

$$\text{div}(\mathbf{D}\nabla c - \mathbf{v}c) - R\lambda c = R \frac{\partial c}{\partial t} \quad (5.15)$$

D_x - Hydrodynamic dispersion coefficient in the x direction (Defined by Bear (1972))

v_x - average linear pore water velocity in the x direction

x - spatial coordinates

t - time

$c = c(x,t)$ - concentration

λ - decay constant;

$$\lambda = (\ln 2) / t_{1/2} \quad t_{1/2} = \text{half-life}$$

R - Retardation factor,

$$R = \left(1 + \frac{\rho_b}{n_e} K_d\right)$$

ρ_b - bulk density of the saturated porous medium, n_e - effective porosity,

K_d - distribution coefficient that governs the partitioning of the solute into dissolved and adsorbed phases.

Numerical Implementation:

$$D_x \frac{(c_{i-1,j,k} - 2c_{i,j,k} + c_{i+1,j,k})}{\Delta x^2} + D_y \frac{(c_{i,j-1,k} - 2c_{i,j,k} + c_{i,j+1,k})}{\Delta y^2}$$

$$+ D_z \frac{(c_{i,j,k-1} - 2c_{i,j,k} + c_{i,j,k+1})}{\Delta z^2} = v \frac{(c_{i,j,k,t} - (c_{i,j,k})t) - \Delta t}{\Delta x} + R\lambda(c_{i,j,k})t + \frac{(c_{i,j,k,t} - (c_{i,j,k})t) - \Delta t}{\Delta t} \quad (5.16)$$

We can write the nodal template form by inspection directly from the difference equation.

Multiplying the difference equation through by the volume $\Delta x \Delta y \Delta z$, and letting

$$a = \frac{D_x \Delta y}{\Delta x}; \quad b = \frac{D_y \Delta x}{\Delta y}; \quad c = \frac{D_z \Delta x \Delta y}{\Delta z}; \quad V = v \Delta x \Delta y \Delta z$$

and $d = 2(a + b + c)$, the finite difference template becomes

$$\underbrace{\begin{bmatrix} -a & -b & -c & d & -c & -b & -a \end{bmatrix}}_{M^D} + \frac{1}{\Delta x} \underbrace{V \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}}_{M^V} - \frac{1}{\Delta t} \Delta x \Delta y \Delta z \underbrace{\begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix}}_{M^S} \begin{Bmatrix} c_{i-1,j,k} \\ c_{i,j-1,k} \\ c_{i,j,k-1} \\ c_{i,j,k} \\ c_{i,j,k+1} \\ c_{i,j+1,k} \\ c_{i+1,j,k} \end{Bmatrix}$$

$$\frac{1}{\Delta x} V(c_{i,j,k})_{t-\Delta t} + R\lambda(c_{i,j,k})_{t-\Delta t} \Delta x \Delta y \Delta z + \frac{1}{\Delta t} \Delta x \Delta y \Delta z (c_{i,j,k})_{t-\Delta t} \quad (5.17)$$

The global matrix equation will become;

$$\left\{ [M^D] + [M^V] + [M^\lambda] \frac{1}{\Delta t} [M^S] \right\} \begin{Bmatrix} c_{i-1,j,k} \\ c_{i,j-1,k} \\ c_{i,j,k-1} \\ c_{i,j,k} \\ c_{i,j,k+1} \\ c_{i,j+1,k} \\ c_{i+1,j,k} \end{Bmatrix} = R\lambda(c_{i,j,k})_{t-\Delta t} + \frac{\Delta x \Delta y \Delta z}{\Delta t} (c_{i,j,k})_{t-\Delta t} \quad (5.18)$$

Where the individual finite difference matrix templates are:

Dispersion matrix

$$[M^D] = [(-a)(-b)(-c), 2(a+b+c)(-c)(-b), (-a)] \quad (5.19)$$

where

$$a = \frac{D_{xx} \Delta y}{\Delta x}; \quad b = \frac{D_{yy} \Delta x}{\Delta y}; \quad c = \frac{D_{zz} \Delta x \Delta y}{\Delta z};$$

Advection matrix (upstream-weighted form)

$$[M^V] = v_x \Delta y [-1, 0, 0, 1, 0, 0, 0] \quad (5.20)$$

Decay matrix

$$[M^\lambda] = R\lambda \Delta x \Delta y \Delta z [0, 0, 0, 1, 0, 0, 0] \quad (5.21)$$

$$[M^S] = R\Delta x\Delta y\Delta z[0..0..0..1..0..0..0] \quad (5.22)$$

This numerical technique entails using an upstream-weighted finite difference scheme for the advection term and an explicit scheme for the dispersion term in the ADE because these schemes were more stable. The method of finite difference was used to solve the 3-D groundwater flow and the Advection-Dispersion equation, while the FORTRAN computer language was used to code the algorithm and develop the *SandModel* computer code. The results were displayed graphically using the MATLAB application package.

Input parameters used for the '*SandModel*' are based on the calibration of ground water flow and contaminant transport for the physical sand tank model and a review of the pertinent literature.

The experimental aquifer was discretized into 336,000 elements, comprising; 80 layers, 140 rows, and 30 columns ($n_i=140$, $n_j=30$, and $n_k=80$). Each grid cell was 1.0cm long by 1.0cm wide. The accuracy of a numerical model is partially governed by the grid spacing and time step constraints. For modeling purposes, the sand tank model was conceptualized as a shallow unconfined aquifer comprised of gravelly sand as porous media material. The specified constant hydraulic heads at the up gradient and down gradient boundaries of the porous medium were 73cm and 68.5cm respectively. Type 1, Fixed concentration at observation well A (OW_A) (Dirichlet) and Type 2, zero concentration or impermeable boundary (Neuman) contaminant transport boundary conditions were used. The input parameters for the model are in Table 5.20.

Table 5.20: Input parameters for the model

Parameter	Value	Source
dispersivity:		Fitting observation to ADE
longitudinal (α_L)	0.07 cm	
transverse (α_T)	0.007cm	
Hydraulic conductivity (K_s)	5.76×10^{-4} m/s	measured
Gradient	0.0321	measured
Effective Porosity (n_e)	0.20	Fitting observation to ADE
Velocity (v)	2.2×10^{-3} m/s	Fitting observation to ADE
Bulk density (ρ_b)	1.9 Mg/m ³	measured
Median grain size (d_{50})	0.55	measured
Injection rate	12 ml/min	Measured
Retardation factor (BTEX) [R]	1.5	Fitting observation to ADE
First-order decay rate (λ) (BTEX)	0.0002/day	Fitting observation to ADE

5.3.5 Model Results and Analysis

The numerical model was run to simulate the observed BTEX breakthrough results. Multiple simulations were completed by adjusting the values of the reactive transport parameters; retardation factor (R) and biodegradation rate to fit the breakthrough data collected at all the twelve observation points. A comparison of the measured and simulated breakthrough profiles for four (4) observation points (OW_{BM}, OW_{CM}, OW_{DM}, OW_{EM}) are shown in Figures 5.37 - 5.40. Statistical comparison of observed and simulated data using the coefficient of determination (R^2), as correlation index and the Paired-t test of significance between sample means at 5% level of significance for the breakthrough curves reveals a high correlation and that there is no significant difference between the observed and simulated data sets. The summary of the statistical analysis for the four observation wells are as follows;

Observation well B [$R^2=0.96$, N=5, Calculated t= 1.311 with df 4, P=0.260 (2-tailed)]

Observation well C [$R^2=0.96$, N=5, Calculated t= 1.445 with df 4, P=0.222 (2-tailed)]

Observation well D [$R^2=0.96$, N=5, Calculated t=0.910 with df 4, P=0.414 (2-tailed)]

Observation well E [$R^2=0.98$, N=5, Calculated t=1.325 with df 4, P=0.256 (2-tailed)]

where; R^2 – Coefficient of Determination
N – Sample size
t - t-statistic(student t quantile) [Table 3. Appendix C]
df – degree of freedom (N-1)

P - calculated probability is the estimated probability of rejecting the **null hypothesis (H_0)** of a study question when that hypothesis is true.

Calculated t value for each well is less than the critical value of t ($t_{critical} = 2.78$ for $df = 4$ [Table 3, Appendix C]), and the calculated P value for each well is greater than the chosen significance level ($P=0.05$), therefore the null (no difference) between observed and simulated data sets hypothesis is accepted. The analysis also reveals a very high correlation between the observed and simulated values. The calibrated estimates of the model parameter that best fit the profiles are the retardation factor (R) value of 1.5 and biodegradation rate of 0.0002/day.

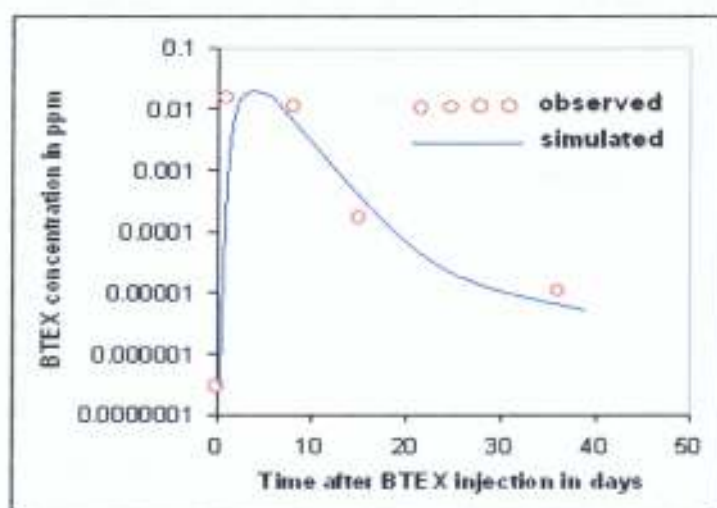


Figure 5.37: Measured and simulated BTEX Breakthrough Curve for observation well (OW_{BM})

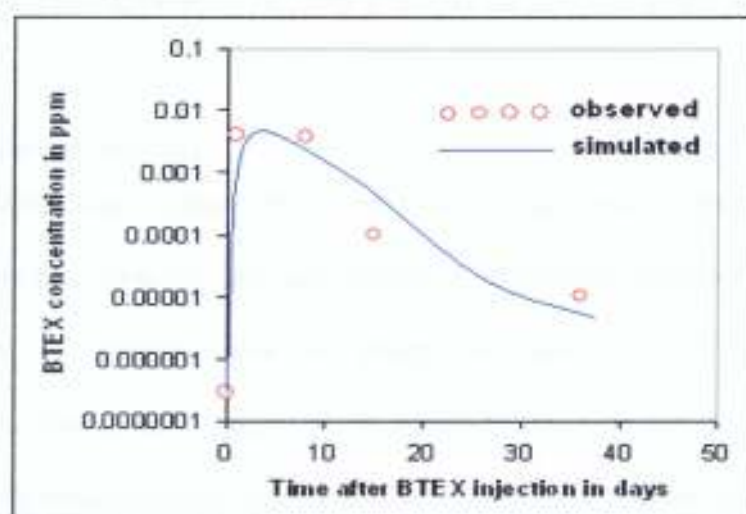


Figure 5.38: Measured and simulated BTEX Breakthrough Curve for observation well (OW_{CM})

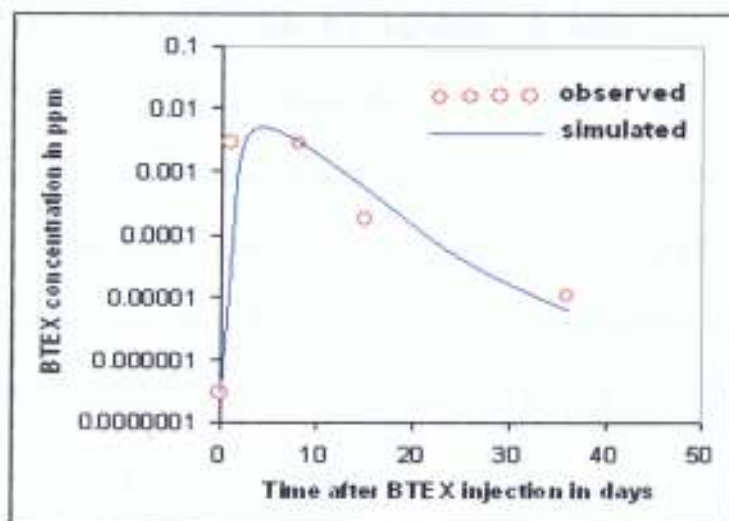


Figure 5.39: Measured and simulated BTEX Breakthrough Curve for observation well (OW_{DM})

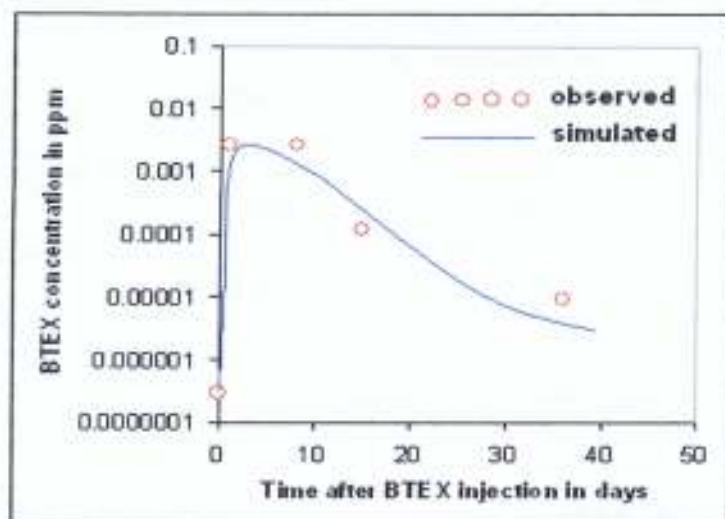


Figure 5.40: Measured and simulated BTEX Breakthrough Curve for observation well (OW_{EM})

5.3.6 Sensitivity Analysis

The base case scenario represents only a single set of system parameter, many of which show considerable variation and uncertainty in published laboratory and field data. Molson and Frind (1990) for example show that parameter uncertainty can lead to non-unique predictive simulations of biodegrading organics. A sensitivity analysis was therefore performed on the base case scenario to determine the influence of several of these parameters on system behaviour.

Scenario 1 considers higher BTEX retardation ($R=15$) which would represent an aquifer material with higher retardation factor and organic carbon fraction. The retarded BTEX plume had a lower peak concentration and returned to near background concentration in twenty four (24) days. For

Scenario 2, in order to evaluate the variations in biodegradation rate values, two additional simulations were completed using the biodegradation rate values 0 and 0.015/day. Zero biodegradation rate represents when there is no biodegradation and 0.015/day is a higher biodegradation rate than the base case scenario. The biodegradation rate was the most sensitive model parameter, with about 82% increase in BTEX maximum plume concentration, for the zero biodegradation scenario. The results for these sensitivity simulations are summarized in Table 5.21 and Figures 5.41 - Figure 5.42.

Table 5.21: Summary of Sensitivity Analysis

Variable	Value	Max. Plume concentration (mg/l)	Δ Concentration with Respect to Base Case
Base Case		1.7×10^{-2}	
Retardation factor (R)	R	1.7×10^{-2}	0%
	10R	1.1×10^{-2}	- 35.3%
Biodegradation Rate λ	0	3.02×10^{-2}	82.2%
	0.015	5.88×10^{-3}	- 65.4%

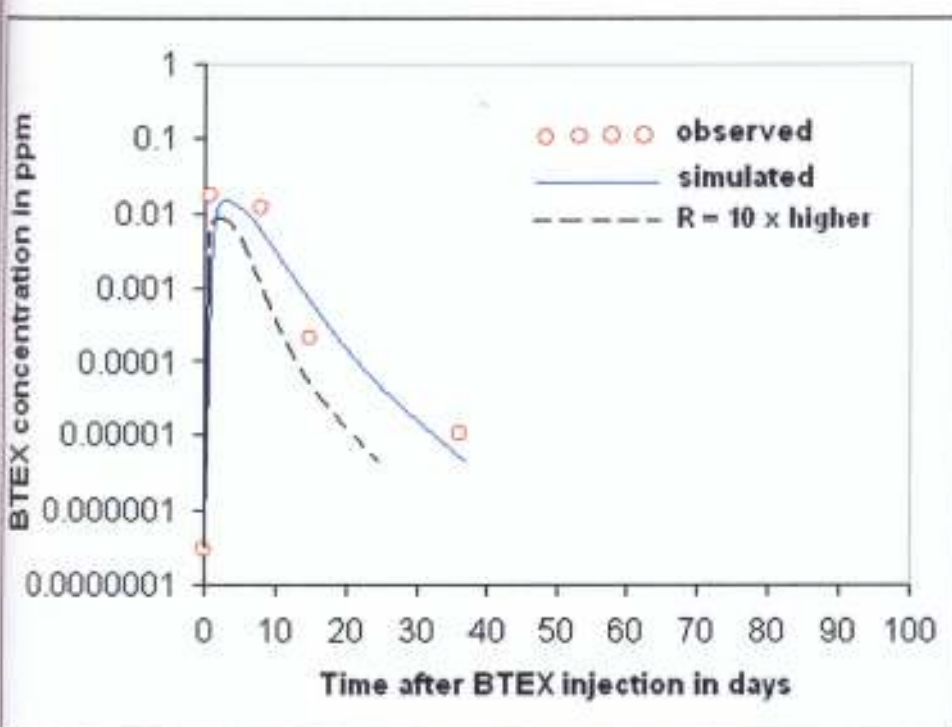


Figure 5.41: Model Sensitivity to Retardation factor (Sampling location OW_{BM})

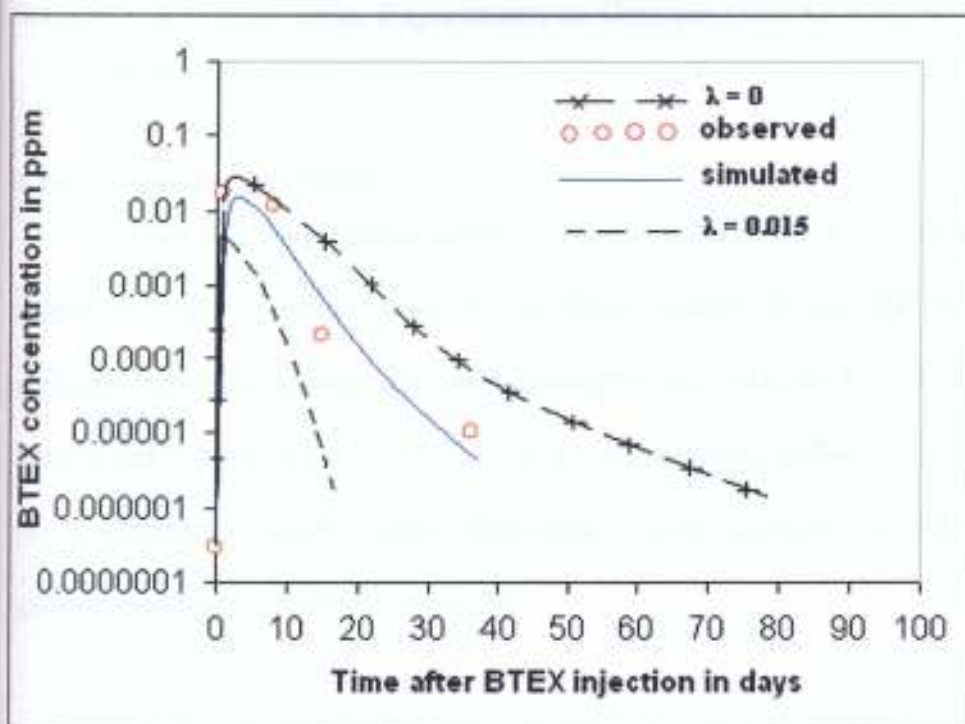


Figure 5.42: Model Sensitivity to Decay constant (Sampling location OW_{BM})

5.4 The Use of Sand Tank Experiments to Simulate Field Conditions at the Contaminated Baruwa, Site.

5.4.1 General overview

For a homogeneous porous medium, ground water moves uniformly through a cross section at a pore velocity equal to the Darcy velocity divided by the total porosity. However, geologic media are almost invariably heterogeneous, particularly at field scale. In this section the three-dimensional (3-D) laboratory scale aquifer modeling technique has been extended and applied to a field-scale study using field-scale model domain, boundary conditions and field geotechnical/hydrodynamic parameters.

5.4.2 Laboratory and field model description

5.4.2.1 Laboratory aquifer model

Numerical simulations were performed to assess the reactive transport and natural attenuation of gasoline fuel components in a 3-D sand tank model. The conceptual model includes a residual gasoline source which is dissolving into the 3-D aquifer. Laboratory sand tank experiments were performed with a medium to coarse sand to determine the NAPL dissolution, fate and transport of dissolved constituent using calibrated seepage velocities and hydrodynamic dispersion parameters. The model showed an excellent fit to the observed data. Calibration is achieved by comparing observed and simulated concentrations of four gasoline fuel components, Benzene, Ethylbenzene and Xylene (BTEX), over a 36-day monitoring period. The biodegradation rate was the most sensitive model parameter, with about 82% increase in BTEX maximum plume concentration, for the zero biodegradation scenario. Details of the laboratory sand tank model design, fabrication, evaluation and computer simulations are available in Sections 5.1 - 5.3.

5.4.2.2 Baruwa field site

The case study site is Baruwa community in Alimosho Local government area of Lagos state (Latitude 6° 35' N, Longitude 3° 16' E). The study site is 940m x 740m in size. The height above the sea level is about 42 m (141 feet). The neighboring towns to the community to the East are Kadara and Akinogun while Fatode and Oduwale are to the south. It has an abundant rainfall of over 2,000 millimeter per year.

The Baruwa community is a predominantly residential setting with population of about 90,000 people. Majority of the people within this area depend on the groundwater for their survival. Many years ago, the people of Alimosho Local Government, that first settled in the community engaged in cash crop and present farming on the area of land that spread on over 100,000 acres. Farming was their main occupation until civilization and development brought in diverse infrastructure to the community. This community suffered from the ruptured underground pipelines of Nigerian National Petroleum Corporation (NNPC)/Pipeline Product Marketing Company (PPMC) between 1994 and 1996. The PPMC pipelines run across the Baruwa village (see Figure 3.3). The leakage went unchecked for several weeks and contaminated the underground water bodies of these areas, polluting wells and boreholes, thus rendering the waters unhealthy for consumption.

5.4.2.3 Approximate field solute transport parameter estimation

Empirical model calibration to site-specific plume monitoring data is the most common method for determining transport parameters in preparation for future predictions (Bibby 1981; Feehley et al. 2000).

A convenient compromise is to derive the solute transport parameters of the porous media based on soil mechanics empirical relations, relating to grain size distribution and hydraulic conductivity properties of the laboratory and field-scale soils. Calibrated values of dispersion coefficient and hydraulic conductivity for the laboratory sand tank model were used together with the geotechnical grading properties of the sand tank and the field site soils for the estimation of the model input

solute transport parameter (hydrodynamic dispersion) for the field site. The proposed empirical relation for the determination of the field dispersivity parameter is:

$$\frac{D_{50(L)}}{D_{50(F)}}\left(\frac{K_{(L)}}{K_{(F)}}\right)=\frac{\alpha_{(F)}}{\alpha_{(L)}} \dots\dots\dots(5.23)$$

where

- $D_{50(L)}$ – median grain size diameter for laboratory soil
- $D_{50(F)}$ – median grain size diameter for field soil
- $K_{(L)}$ – hydraulic conductivity for laboratory soil
- $K_{(F)}$ – hydraulic conductivity for field soil
- $\alpha_{(L)}$ - dispersivity for laboratory soil
- $\alpha_{(F)}$ - dispersivity for field soil

Using equation 5.23 for laboratory model and Baruwa field site;

- $D_{50(L)} = 0.55$ (Section 5.1)
- $D_{50(F)} = 0.25$ (measured)
- $K_{(L)} = 5.76 \times 10^{-4}$ m/s (Section 5.1)
- $K_{(F)} = 3.2 \times 10^{-6}$ m/s (measured)
- $\alpha_{(L)} = 0.07$ (Section 5.1)
- $\alpha_{(F)}$ - dispersivity for field soil

$$\frac{0.55}{0.25}\left(\frac{5.76 \times 10^{-4}}{3.2 \times 10^{-6}}\right)=\frac{\alpha_F}{0.07}$$

$$\alpha_F = 27.7m$$

The ratio of transverse to longitudinal dispersivity is taken as 0.3. This is to satisfy the condition of heterogeneity at the field-scale (Sudicky, 1986).

5.4.2.4 Numerical Implementation

The method of finite difference was used to solve the 3-D groundwater flow and the

Advection-Dispersion equations, while the FORTRAN computer language was used to code the algorithm and develop the Field-scale *SandModel* computer code. The results were displayed graphically using the MATLAB application package (see Figures 5.4.7 - 5.4.11).

Input parameters (see Table 5.22) used for the Field-scale ‘*SandModel*’ are based on the calibration of ground water flow and contaminant transport for the physical sand tank model, field measurements and a review of the pertinent literature.

The model domain was a rectangular area of 700 x 900 by 5.0m for the field-scale *SandModel*.

The experimental aquifer was discretized into 10,500 elements, comprising; 10 layers, 30 rows, and 35 columns ($n_i=30$, $n_j=35$, and $n_k=10$) (see Figure 5.43). Each grid cell was 30.0m long by 20.0m wide. A time step of 0.5 days was used for the transport simulations.

The accuracy of a numerical model is partially governed by the grid spacing and time step constraints.

The grid spacing satisfies the grid Peclet constraints; $P_x = \frac{v_x \Delta x}{D_{xx}} \leq 2$

In the temporal domain, the time step satisfied the Courant criteria given by $C_x = \frac{v_x \Delta t}{\Delta x} \leq 1$

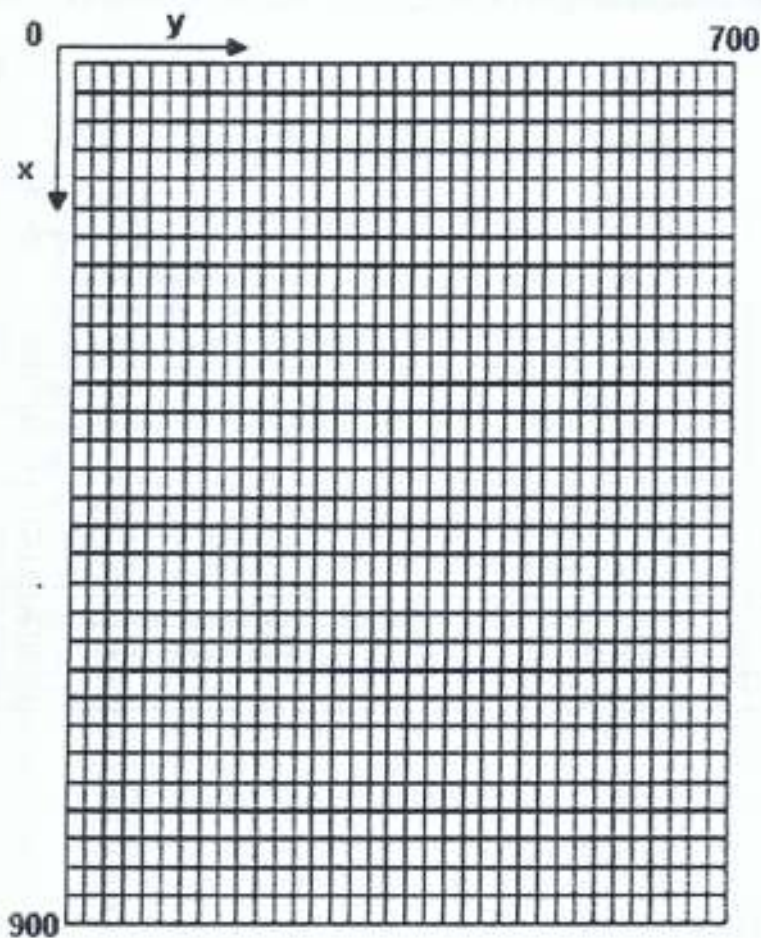


Figure 5.43: Finite difference grid for the Field-scale model

5.4.2.5 Boundary and initial conditions

The conceptual model is a residual gasoline source which is dissolving at the water table into the 3-D aquifer, comprised of silty sand as porous media material. The hydraulic gradient across the site was 0.004 (Adekunte, 2008). Continual recharge of petroleum hydrocarbon to the existing plume is likely due to the activity and age of the facility. Type 1, Fixed concentration around W20 (Dirichlet) and Type 2, zero concentration or impermeable boundary (Neuman) contaminant transport boundary conditions were used. The residual gasoline source is dissolving around Well 20 (W20) into the 3D aquifer. Pure phase petroleum product (Non-aqueous phase liquid) [NAPL] released from the ruptured underground NNPC pipeline in 1994 remains entrapped in the soil around W20, and continues to dissolve at the water table into the aquifer. Table 5.22 shows the input parameters for the model. Field measurements of petroleum hydrocarbon concentration at the Baruwa site reveal the highest concentrations at well 20 and well 10. The physico-chemical properties of the gasoline components used in the model are presented in Table 5.23.

Table 5.22: Input parameters for the model

Parameter	Value	Source
dispersivity:		Approximation based on Lab./Field Scale empirical relation
longitudinal (α_L)	27.7 m	
transverse (α_T)	8.3m	
Hydraulic conductivity (K_x)	3.2×10^{-6} m/s	Measured
Gradient	0.004	Measured (Adekunte 2008)
Porosity (n)	0.41	Measured
Velocity (v)	1.28×10^{-8} m/s	Measured
Bulk density (ρ_b)	1.86 Mg/m ³	Measured
Median grain size (d_{50})	0.25	Measured
Injection concentration	872g/l	Fitting observation to ADE
Retardation factor (BTEX) [R]	2.5	Fitting observation to ADE
First-order decay rate (λ) (BTEX)	0.0004/day	Fitting observation to ADE
Simulation period	12 years	Literature review

Table 5.23: Properties of the gasoline components

Compound	MW ⁽¹⁾ (kg/mole)	Pure Phase Solubility ⁽¹⁾ (kg/m ³)	Density ⁽²⁾ (kg/m ³)	Diffusion Coefficient ⁽¹⁾ (m ² /s)
Benzene	0.078	1.780	878.6	7.7e-10
Toluene, Ethylbenzene, Xylene (TEX)	0.104	0.288	870.0	6.2e-10

MW – Molecular Weight

¹ Wiedmeier et al. (1999), Appendix B

² CRC Handbook of Chemistry and Physics (1980)

5.4.2.6 Analytical procedures

Ground water samples were collected into 40ml glass bottles using a bailer. The samples were kept below 4°C, using ice packs. Concentration profiles were measured for twenty five wells in September 2006 and December 2006. The samples were transported to the Multi-Environmental laboratory Ketu, Lagos for both organic (BTEX) and inorganic analyses.

The parameters analyzed for the groundwater include; Benzene, Toluene, Ethylbenzene, and Xylene (BTEX), light-end components of gasoline, and are of most concern from an environmental impact perspective; Dissolved oxygen (DO), Nitrate (NO₃), and Sulphate (SO₄), (electron acceptors); Ferrous iron (Fe⁺²), and Manganese (Mn⁺²), bi-products of biological activity.

The BTEX components of gasoline and benzene in particular, are of primary concern because of their relatively high solubility and toxicity at low concentrations.

The gas chromatography apparatus (GC) HP5890, powered with HPCHEM software was used for the BTEX analysis. 10mls of water sample was transferred into the headspace sampler for analysis, using a flame ionization detector (FID). The chromatography was electronically integrated and peak area obtained for a particular BTEX component. A calibration curve was made of concentration against peak area and a response factor obtained for each component. The metal ions in ground water samples (Mn⁺² and Fe⁺²) were determined using Inductively Coupled Plasma Emission Spectrometry apparatus.

5.4.3 Results and analysis

5.4.3.1 Periodic field sampling and analysis (BTEX)

Table 5.24 is a summary of the groundwater BTEX concentration measurements for twenty five wells at the field site. These measurements were taken during this research with the aid of field assistants. Highest BTEX concentrations of 106.11mg/l and 77.82mg/l were obtained at well 20 for the 1st (September, 2006) and 2nd sampling sessions (December, 2006) respectively. The isoconcentration contours are in Figures 5.44 & 5.45. Adekunle (2008) obtained a similar hydrocarbon concentration contour for the Baruwa site in June 2006 (see Figure 5.46). Figures 5.47 and 5.48 (after Adekunle 2008) show the direction of ground water flow derived from depth to water table contours and the contour of liquid hydrocarbon thickness above water surface.

Table 5.24: Groundwater BTEX Concentration in twenty-five (25) Wells at Baruwa

TOTAL BTEX CONCENTRATION (mg/l)		
WELL LOCATION	1 ST SESSION (SEPT. 2006)	2 ND SESSION (DEC. 2006)
Well 20	106.11	77.82
Well 10	104.04	75.50
Well 41	65.00	48.00
Well 44	61.70	45.03
Well 42	62.00	35.00
Well 45	61.95	40.62
Well 48	56.08	45.24
Well 73	30.63	22.30
Well 51	20.49	14.34
Well 64	26.50	20.04
Well 75	33.02	17.90
Well 157	25.20	21.68
Well 159	24.24	21.80
Well 14	22.60	18.20
Well 144	22.30	17.39
Well 155	22.00	17.50
Well 143	21.20	17.00
Well 140	20.60	16.50
Well 13	20.50	15.30
Well 14	20.00	14.00

Well 15	20.00	15.90
Well 168	19.90	18.00
Well 139	19.60	13.00
Well 162	13.90	11.10
Well 136	12.00	10.30

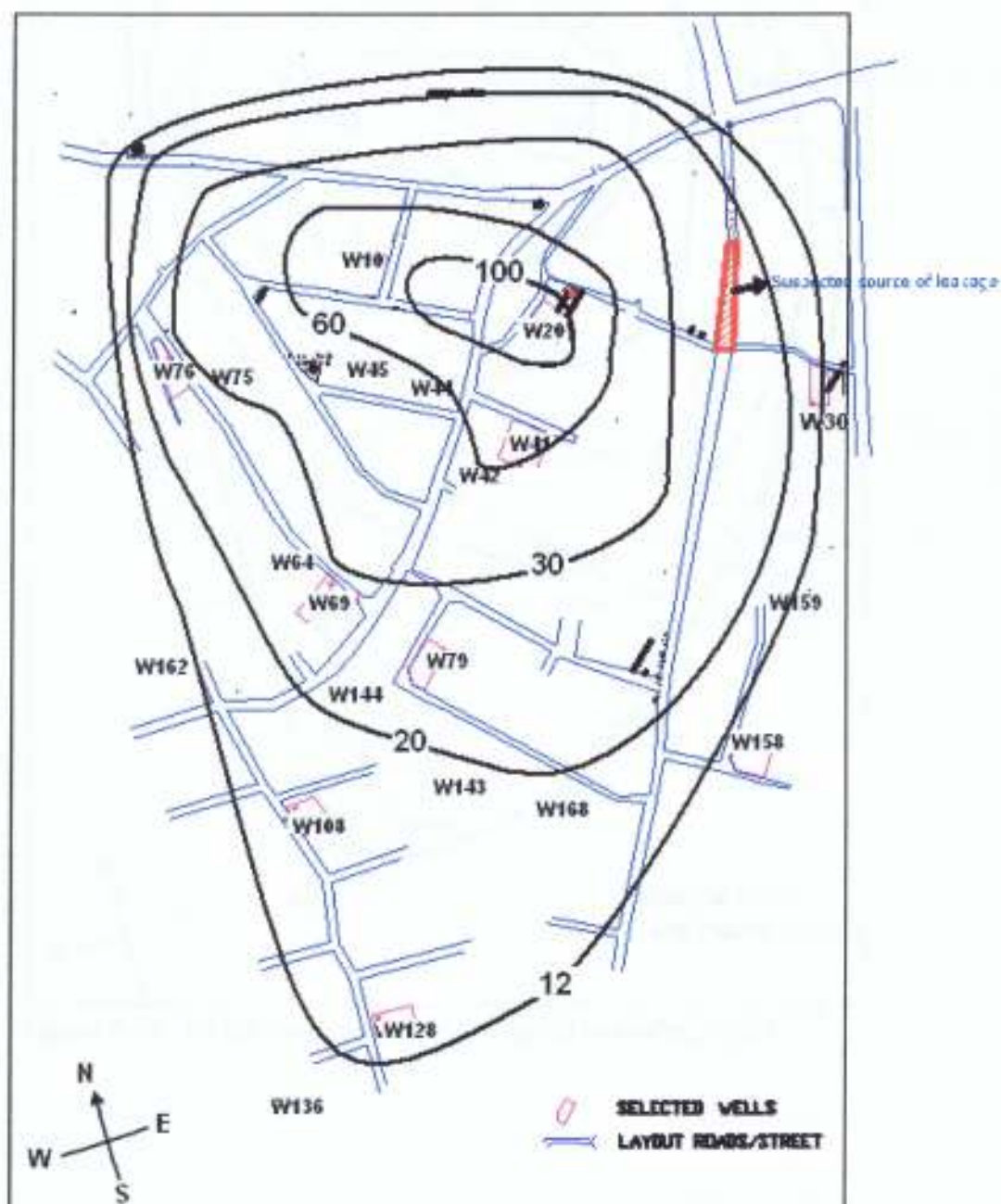


Figure 5.44: BTEX Isoconcentration -mg/l [September, 2006]

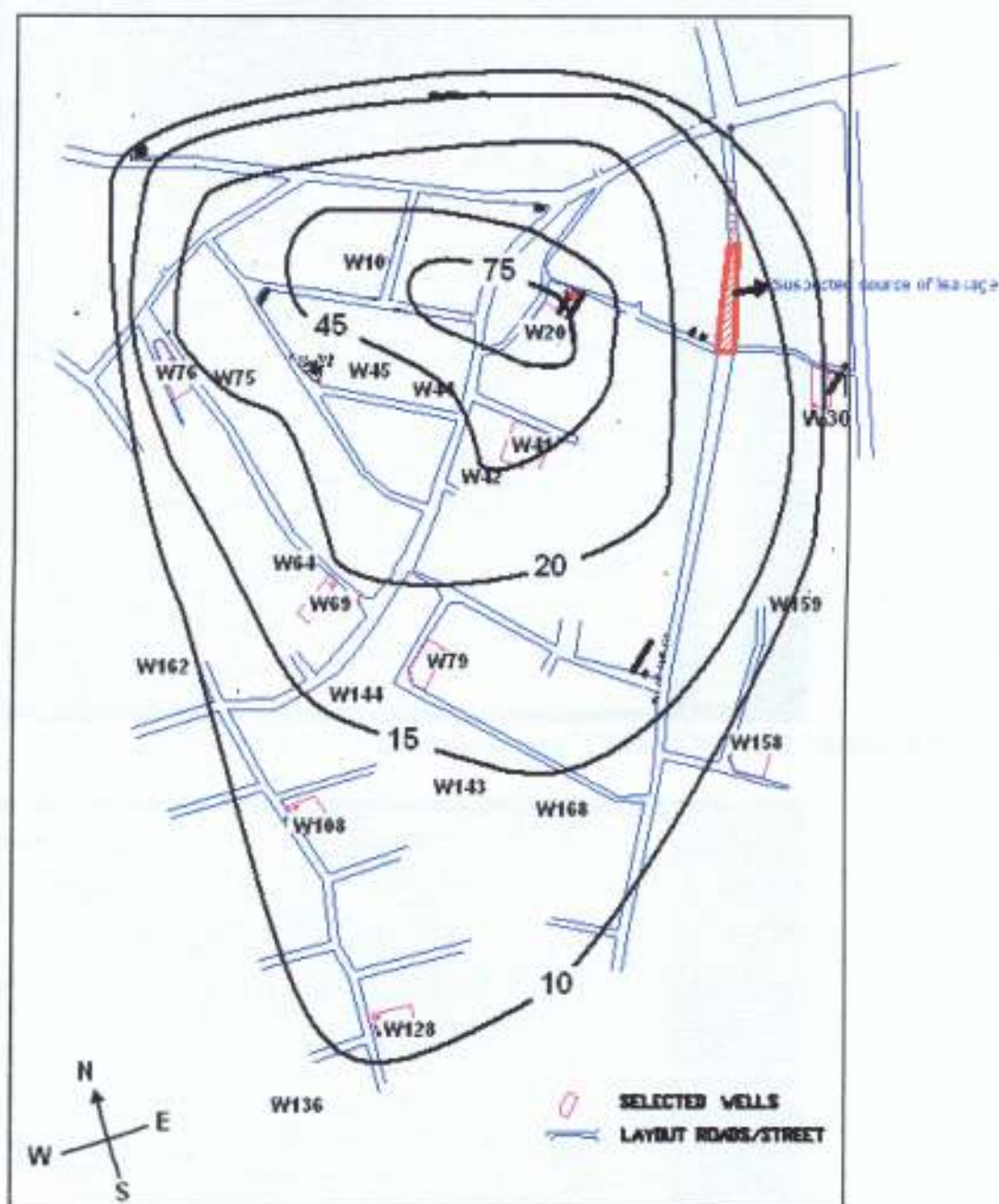


Figure 5.45: BTEX Isoconcentration -mg/l [December, 2006]

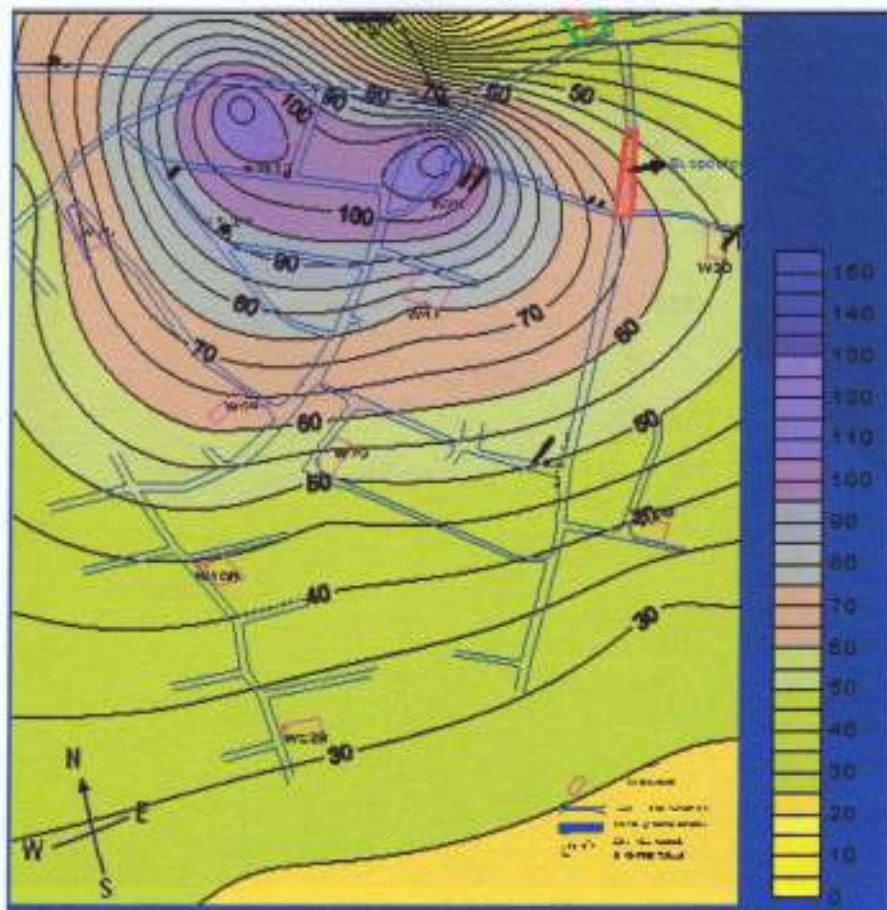


Figure 5.46: Total Hydrocarbon Isoconcentration -mg/l [June, 2006] (Adekunte, 2008)

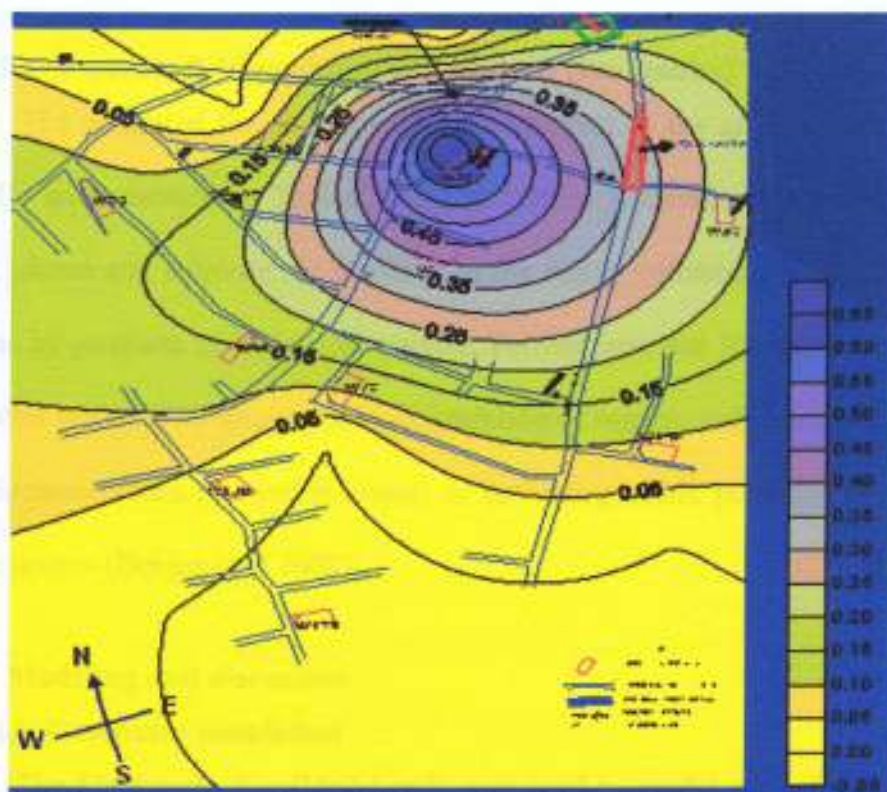


Figure 5.47: Liquid Hydrocarbon Thickness above Water Surface (m) [June, 2006] (Adekunte, 2008)

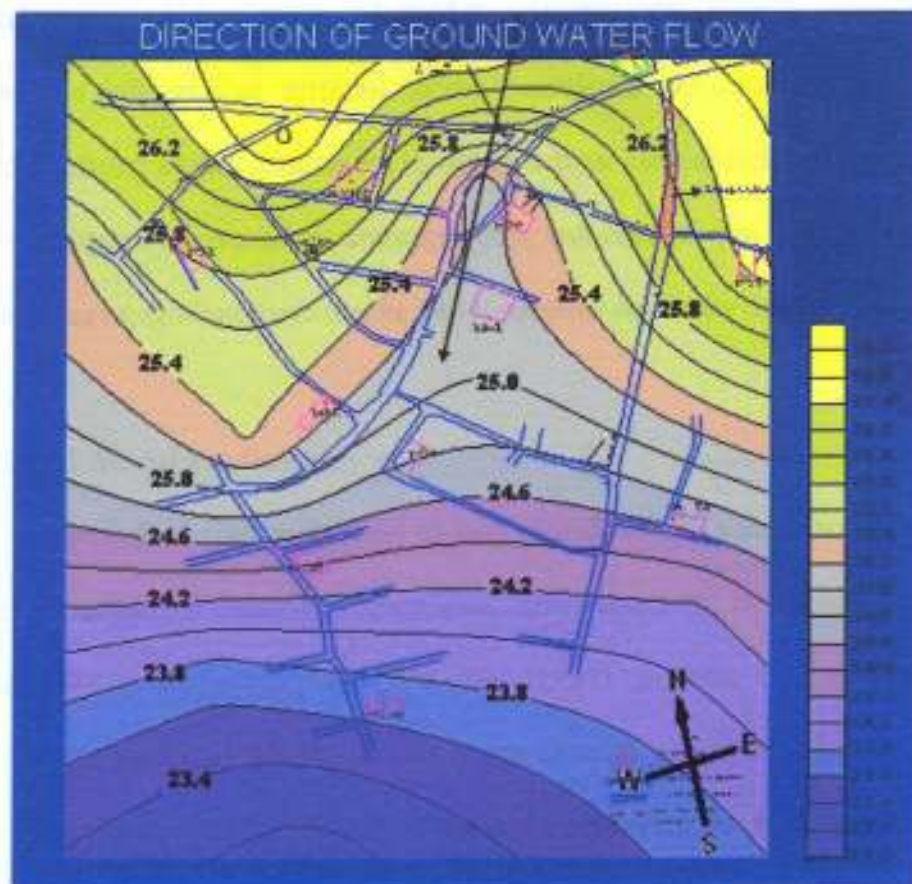


Figure 5.48: Direction of Ground Water Flow (Adekunte, 2008)

5.4.3.2 Periodic field sampling and analysis (Inorganics)

The results of the physico-chemical analyses of the groundwater samples for the twenty five wells are presented in Tables 5.25 and 5.26 in Appendix A1. Electron acceptors; dissolved oxygen, nitrate and sulphate are depleted in the highly contaminated wells W20, W10, W41 etc., while the by products of biological activity; Ferrous iron and Manganese increased in comparison to the other wells. With long-term biodegradation of organic pollutants in groundwater, a sequence of geochemical zones (or redox zones) of increasing redox potential will develop downgradient from the source (Bekins et al 2002).

5.4.4 Modeling and discussion

5.4.4.1 Computer simulation

The Field-scale *SandModel* code was used to model groundwater flow and transport of organic contaminants [Benzene, Ethylbenzene, Toluene, Xylene (BTEX)] in the subsurface for the area of case study. The numerical model was used to study the conceptual model of the study area.

The boundaries of the numerical model coincide with natural hydrogeologic boundaries to minimize the influence of artificial model boundaries on simulation results. Model calibration involved adjusting model parameters to obtain a reasonable match between observed and simulated output variables. Patterns of groundwater flow and contaminant flux were predicted by the model with a view to integrating these results into a remedial feasibility design.

5.4.4.2 Model Predictions

One method commonly used to help identify NAPL source zones, and source history is to analyze periodically, dissolved component concentrations in monitoring wells. Johnson and Pankow (1992); Anderson and Woessner (1992) describe the use of downgradient solute concentrations to locate NAPL source zones through the application of physical and analytical models. The source zone location is estimated by observing the well pattern distribution, noting the localized ground water flow patterns, and backtracking upgradient against the direction of ground water flow. Computer simulations based on measured hydrogeologic properties such as hydraulic conductivity (or permeability), hydraulic gradient, and velocity has been used to generate backtracking simulations for the approximate source history of the contaminated field site.

The injection period was set at 1994 by model calibration. The (total) BTEX plumes are shown in plan view (through the source centre) at 0.5, 12, 20, 40 and 60 years in Figure 5.49 – Figure 5.53. At six months (6 months after injecting BTEX of 872 g/l), the simulated plume attained a steady state configuration with source dissolved concentration of about 550mg/l (Figure 5.49). The injected total BTEX concentration of 872g/l for the field-scale model was obtained by model calibration/back calculation and fitting the field hydrocarbon concentration observations to the simulated hydrocarbon isoconcentration contours for the period of field sampling and testing (year 2006). To obtain the injected/released hydrocarbon concentration, that fits the site contamination history of twelve years from 1994 to the sampling and field testing period (2006), several total BTEX injected concentrations were tried on the Computer simulation model (Table 5.27). These

tested injection concentration values are multiples of the approximate average density of the hydrocarbon contaminant (BTEX). The injected concentration of 872 g/l was able to simulate in twelve years the maximum observed hydrocarbon concentration (100 mg/l) in well 20 during the year 2006 of field sampling and testing (Figure 5.50). Simulation plots for other tested injection concentration values (87.2g/l and 8720g/l) for 6 months and twelve years simulation periods are in Appendix D.

Table 5.27: Injected BTEX concentrations for Field-Scale Model and Simulation Results

Simulation Time (years)						
0	(Injected Concentration)	87.2 g/l	436 g/l	872 g/l	4360 g/l	8720 g/l
0.5	(Max. Observed Concentration)	105 mg/l	200 mg/l	550 mg/l	1020 mg/l	1800 mg/l
12	(Max. Observed Concentration)	18 mg/l	45 mg/l	100 mg/l	430 mg/l	730 mg/l
20	(Max. Observed Concentration)			35 mg/l		
40	(Max. Observed Concentration)			10 mg/l		
60	(Max. Observed Concentration)			0.5 mg/l		

Figure 5.50 shows the observed and simulated systems for 12 years after injection (2006). The simulated contours are in good agreement with the observed plume. Although the observed plume appears to be somewhat wider than the simulated plume, this is possibly an artifact due to the source injection method in the simulated system and the monitoring well spacing and contour interpolation between monitors. Figure 5.53 reveals from the simulations that a chosen clean-up target of 0.5mg/l for BTEX would be reached by the year 2054 with natural attenuation. This is sixty (60) years from the time of hydrocarbon release and forty-eight (48) years from the time of field measurements in 2006.

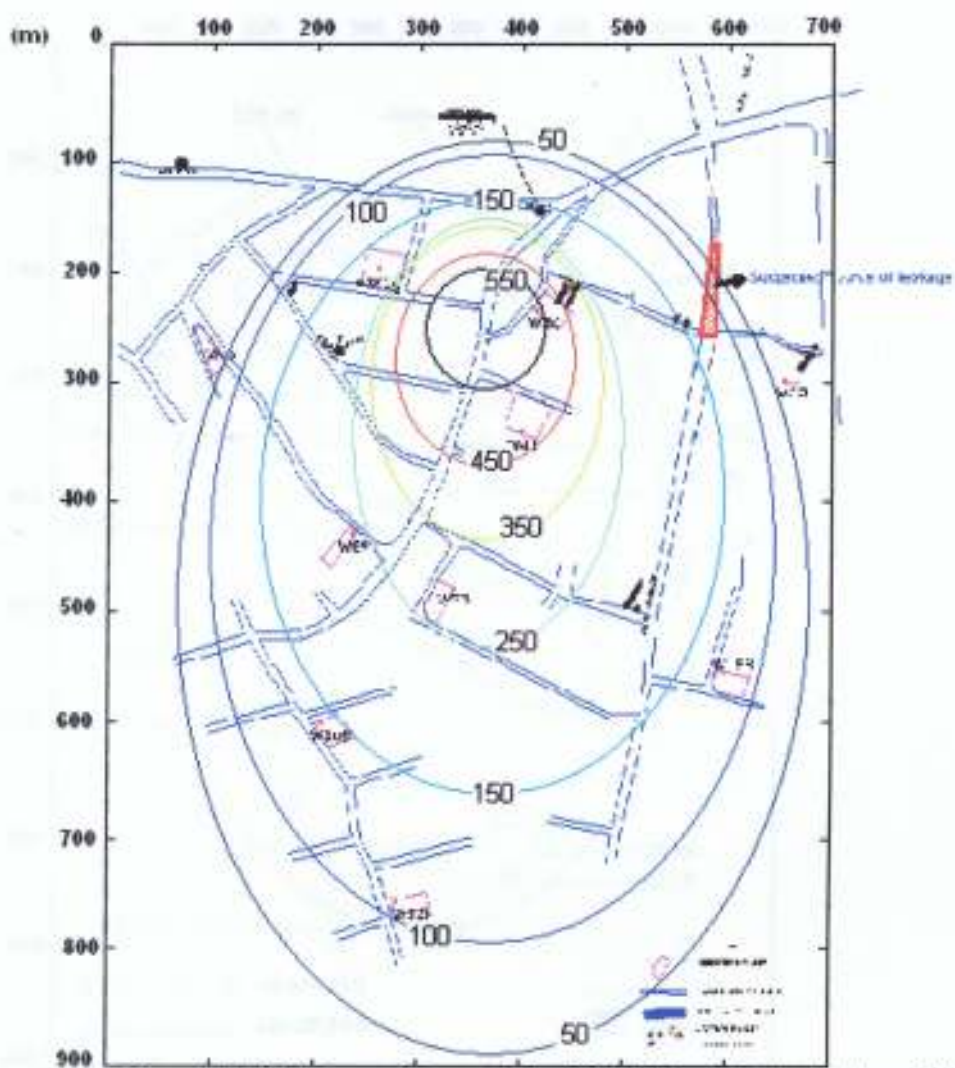


Figure 5.49: 0.5 year [6 months] of BTEX (mg/l) simulation (1994)

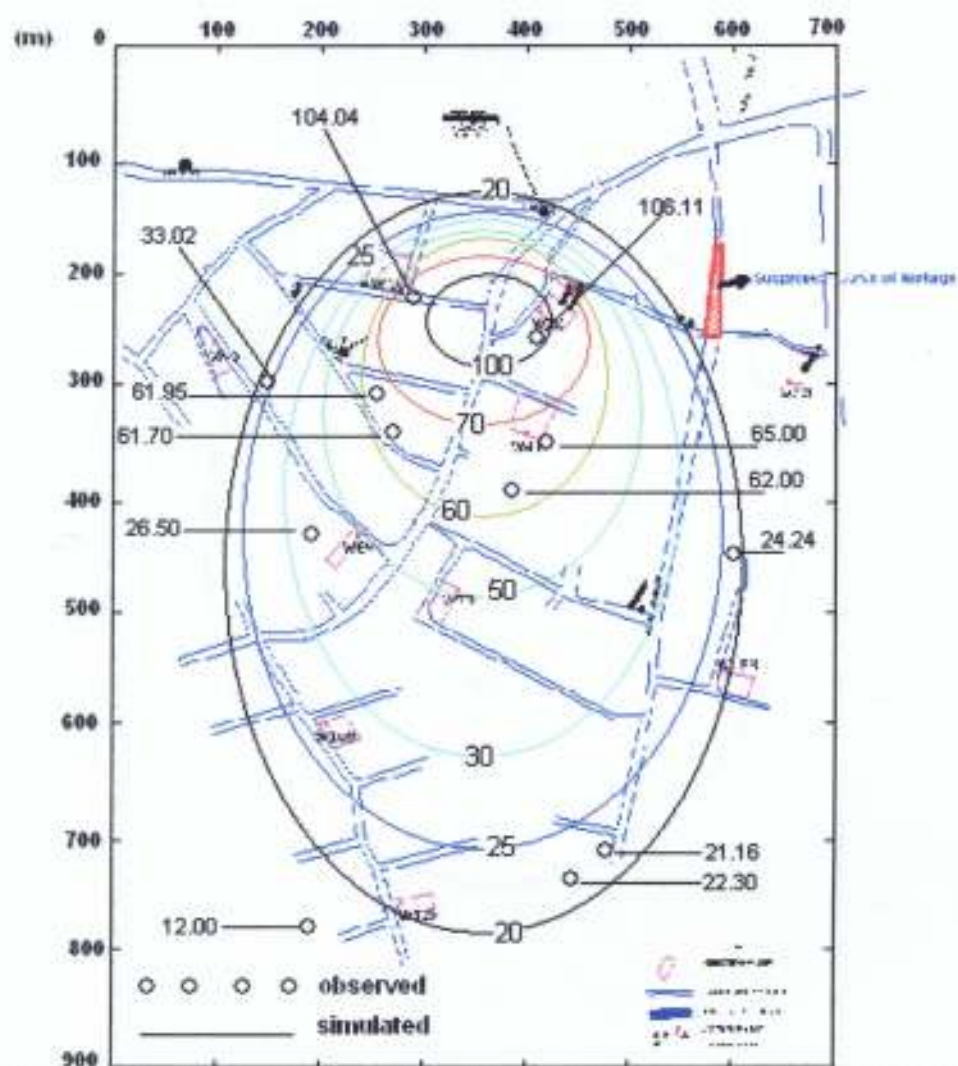


Figure 5.50: A Comparison of Simulated (contoured) and Observed (symbols) BTEX Concentration in the x-y Plane for 12 years of Simulation (2006)

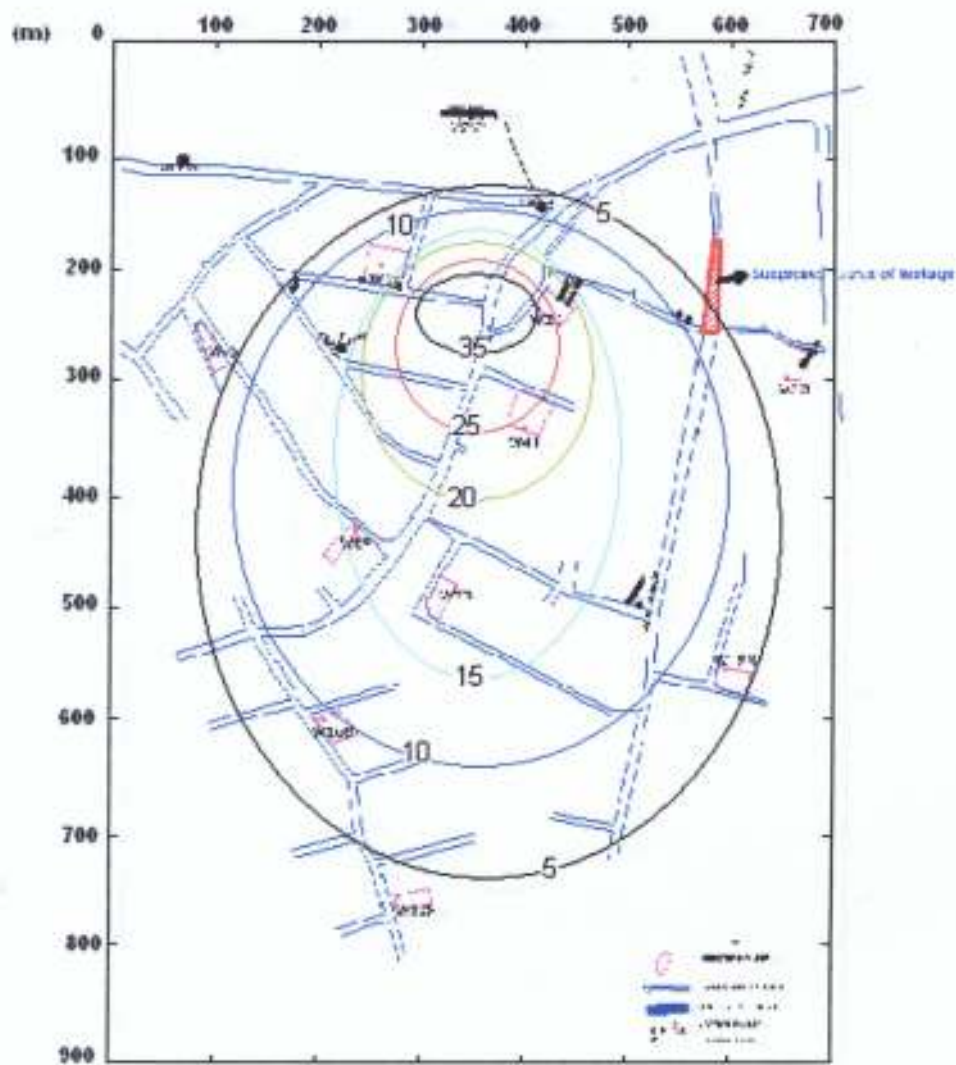


Figure 5.51: 20 years of BTEX (mg/l) simulation (2014)

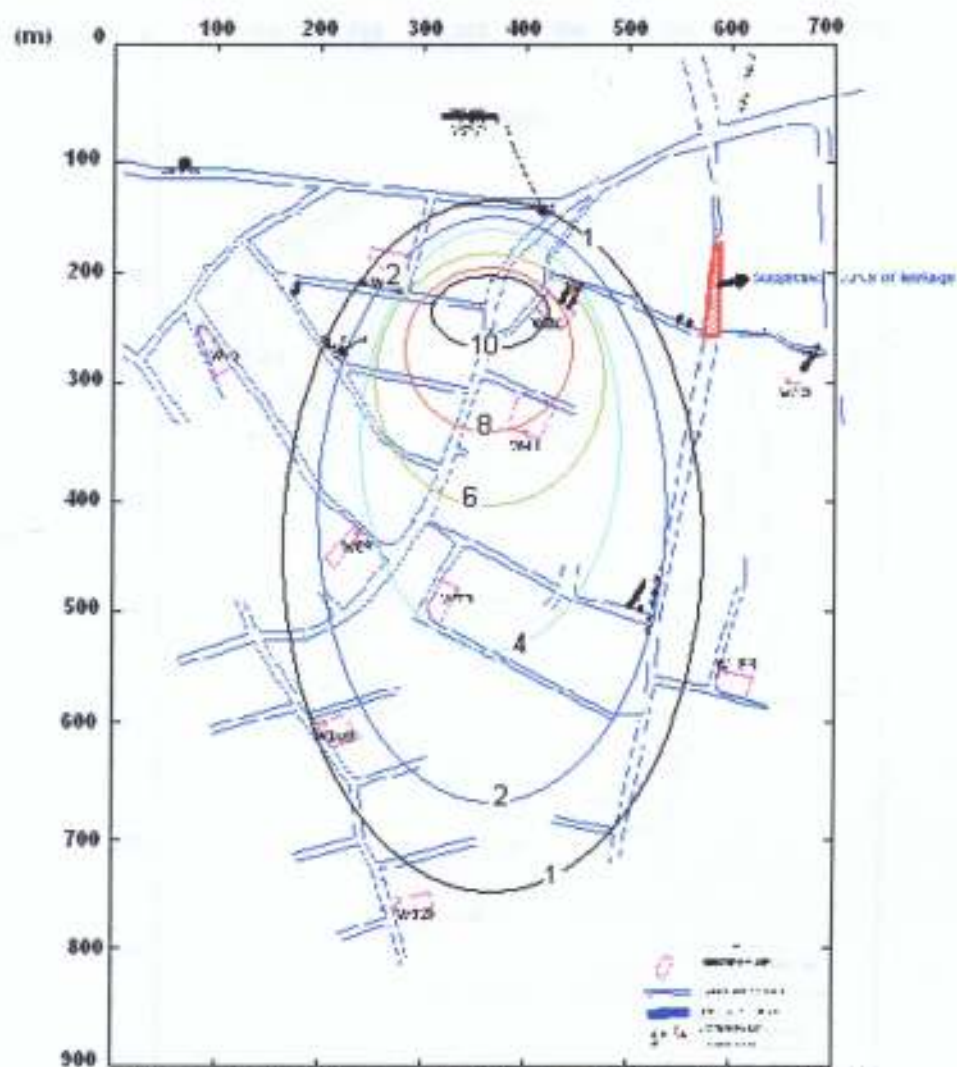


Figure 5.52: 40 years of BTEX (mg/l) simulation (2034)

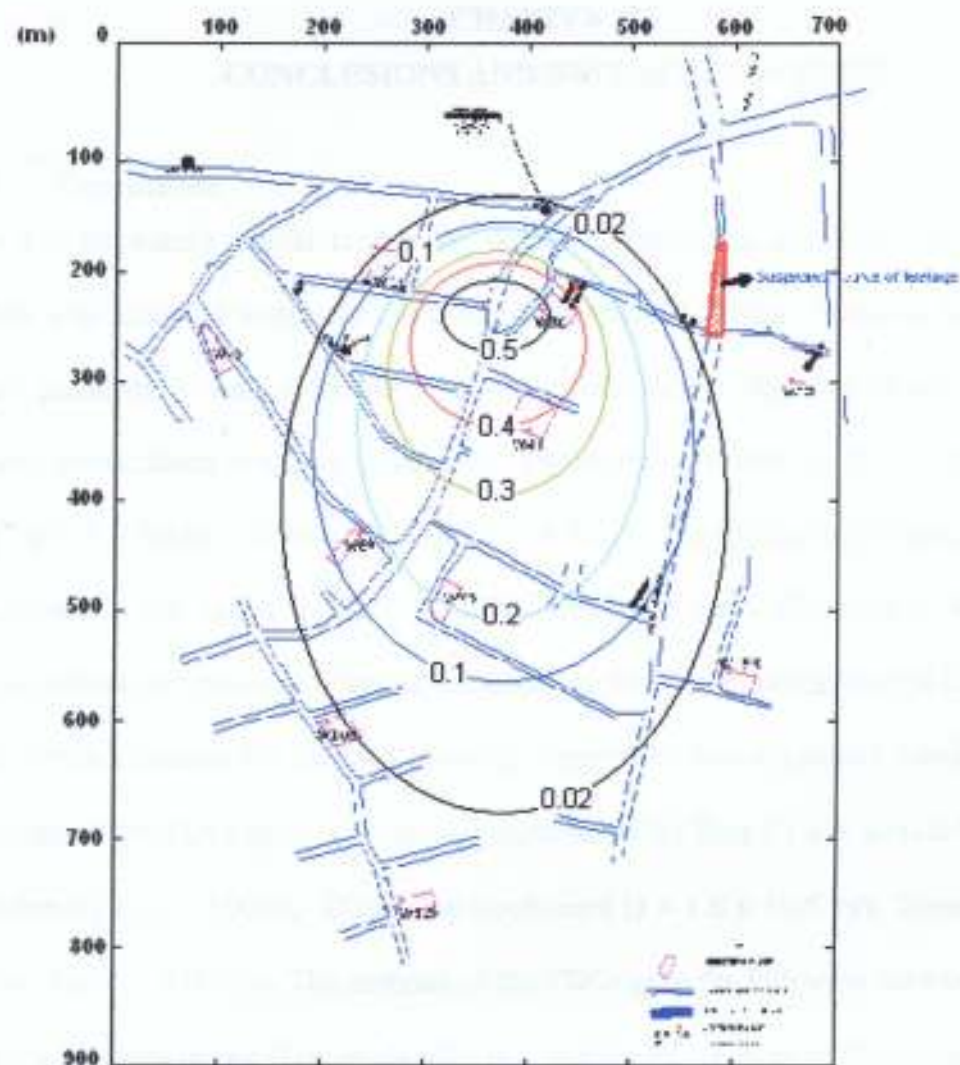


Figure 5.53: 60 years of BTEX (mg/l) simulation (2054)

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

A 3-D laboratory aquifer model was designed, fabricated, assembled and evaluated. Steady state flow was achieved under the quasi-natural gradient condition. Physical, hydraulic and solute transport parameters were established for the southwestern Nigerian Owena sand. This study established contaminant transport parameters: Hydraulic conductivity, $K = 5.76 \times 10^{-4}$ m/s, Bulk density, $\rho = 1.9 \text{ Mg/m}^3$, Effective Porosity, $n_e = 0.215$. The hydraulic gradients for the Sand Tank Model, varies in the range 0.0321 – 0.1393, Discharge rates (Q), 58.0 – 405.0 ml/min. The analytical method of statistical temporal moments of the Tracer Breakthrough Curves (TBCs) was used, to obtain estimates for the flow velocity, dispersivity and dispersion coefficient respectively. The analyses of the TBCs gave the following parameters for Port 1 ($v = 4.13 \times 10^{-6} \text{ m/s}$); Dispersivity (Longitudinal) [α_L] = 0.06cm, Dispersion Coefficient $D = 1.6 \times 10^{-6} \text{ m/s}$, Dispersivity (horizontal transverse) [α_T] = 0.006cm. The analyses of the TBCs gave the following parameters for Port 2 ($v = 1.14 \times 10^{-5} \text{ m/s}$); Dispersivity (Longitudinal) [α_L] = 0.16cm, Dispersion Coefficient $D = 6.9 \times 10^{-6} \text{ m/s}$, Dispersivity (horizontal transverse) [α_T] = 0.016cm.

The developed computer application package *SandModel* was used to simulate the transport of an inorganic tracer (Chloride) and organic (petroleum hydrocarbon) contamination in the laboratory aquifer model and at the Baruwa field site. The simulation results were visualized with the MATLAB application package. The modeling analysis identified two critical model parameters that include the porous media hydraulic conductivity, and the source concentration.

With the laboratory, field and modeling studies, the contaminated site is now basically characterized with water table contour maps/direction of groundwater flow, liquid hydrocarbon thickness contour map, periodic hydrocarbon isoconcentration maps, periodic geochemical parameter test data and geotechnical/statigraphic profiles from geophysical and geotechnical data. This has enabled delineation of the contaminated zone, identification of the likely source of

hydrocarbon contamination and the estimation of the likely subsurface contamination clean-up time with passive natural attenuation. It was revealed from the simulations that a chosen clean-up target of 0.5mg/l for BTEX would be reached by the year 2054 with natural attenuation. This is sixty (60) years from the time of hydrocarbon release and forty-eight (48) years from the time of field measurements in 2006. There is the need to combine both active and passive remediation technologies for this site, in order to achieve timely clean up of the BTEX contamination.

This work presents a modeling framework for integrating a laboratory sand tank model within a large-scale reactive transport code. Soil particle size (D_{50}) and hydraulic conductivity (K) data were used to establish a correlation between the hydrodynamic transport parameters (Dispersivity [α]) for the laboratory and field porous media soils. The proposed empirical relation for the determination of the field dispersivity [α] parameter is;

$$\frac{D_{50(L)}}{D_{50(F)}} \left(\frac{K(L)}{K(F)} \right) = \frac{\alpha(F)}{\alpha(L)}$$

It is concluded that the integrated reactive transport model, is a useful tool for modeling the behaviour of groundwater plumes evolving from entrapped NAPL sources. A Retardation factor $R = 2.5$, and biodegradation rate of 0.0004/day (half life of 5 years) were obtained from the model calibration for BTEX.

6.2 Recommendations

The properly characterized sand tank model will serve as an economic and versatile tool for simulating and understanding field conditions of soil/ground water contamination for similar aquifer materials in Nigeria. Further detailed study on the availability and characterization of the chosen experimental sand (Owena sand) with a comparative study on the renowned experimental Ottawa sand in Canada and the U.SA is recommended.

Remedial feasibility design for the removal of the hydrocarbon source and remediation of the contaminated site using pilot scale field experiments is recommended with the integration of

active and passive remediation techniques for the petroleum hydrocarbon contaminated site in Baruwa. Free-hydrocarbon recovery systems comprising of oil skimmer pumps, oil/water separation tank, pipe fittings, and monitoring mechanical and electronic instrumentation for studies in contaminant recovery systems design and implementation should be used. The remediation programme should include design and fabrication of physical models for the evaluation of the combination of various remediation techniques (both proven and innovative/low-cost technologies) using 1-D column and 3-D aquifer model experiments. It should consist of plexi-glass 1-D cylindrical columns, glass/plexi-glass 3-D sand tanks, over head water reservoir, multilevel sampling pipes and ports, pipe fittings and control/instrumentation systems for the measurement of soil/groundwater hydraulic and geochemical parameters. Such a facility would enhance the development of selection criteria for adopting remediation procedures to contaminated soil/groundwater problems in Nigeria. It would also lead to the optimal design and testing of life cycle treatment systems with in-situ and ex-situ treatment techniques using pilot scale field experiments.

In the situation of petroleum hydrocarbon contamination in Baruwa community, Iyana Ipaja, Lagos, the Nigerian government and in particular the Nigerian National Petroleum Corporation (NNPC) must be seen to be actively involved both in the provision of alternative portable water supply sources to the community and the implementation of a cost-effective soil/groundwater clean-up using appropriate remediation technologies.

Further studies on the use of finite element method in the numerical modeling of the Advection-Dispersion equation for the laboratory and field site will allow for improved boundary conditions and a more robust model.

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TABLE 5.1: RESULT OF SIEVE ANALYSIS OF OWENA SAND

Particle Size (mm)	Percentage Finer Sample A	Percentage Finer Sample B	Percentage Finer Sample C	Percentage Finer Average
2.360	94.1	94.4	95.8	94.8
1.700	87.1	87.4	89.8	88.1
1.180	76.2	78.2	79.3	77.9
0.600	44.3	52.2	51.0	49.2
0.500	37.1	44.0	42.9	41.3
0.425	27.2	34.6	31.6	31.1
0.212	6.3	9.0	6.6	7.5
0.150	2.4	3.2	2.2	2.6
0.075	0.5	0.6	1.1	0.7

Table 5.25: Groundwater Inorganic Analysis in twenty-five (25) Wells at Baruwa (September, 2006)

WELL LOCATION	FERROUS IRON (ppm)	MANGANESE (ppm)	NITRATE (ppm)	SULPHATE (ppm)	DO (ppm)
Well 20	1.633	0.420	0.250	0.038	0.000
Well 10	1.395	0.360	0.330	0.041	0.010
Well 41	0.705	0.210	0.352	0.044	0.000
Well 44	0.685	0.230	0.352	0.043	0.010
Well 42	0.680	0.230	0.350	0.044	0.011
Well 45	0.685	0.240	0.353	0.041	0.010
Well 48	0.645	0.230	0.350	0.042	0.011
Well 73	0.595	0.213	0.364	0.045	0.014
Well 51	0.575	0.210	0.360	0.043	0.015
Well 64	0.548	0.211	0.362	0.042	0.015
Well 75	0.545	0.213	0.364	0.045	0.014
Well 157	0.443	0.211	0.368	0.045	0.026
Well 159	0.440	0.211	0.364	0.045	0.028
Well 14	0.321	0.200	0.380	0.047	0.030
Well 144	0.305	0.210	0.388	0.051	0.042
Well 155	0.305	0.200	0.390	0.051	0.044
Well 143	0.308	0.200	0.392	0.053	0.044
Well 140	0.305	0.201	0.392	0.052	0.044
Well 13	0.255	0.200	0.430	0.057	0.058
Well 14	0.246	0.200	0.431	0.053	0.057
Well 15	0.223	0.200	0.432	0.053	0.059
Well 168	0.200	0.200	0.440	0.057	0.068
Well 139	0.194	0.201	0.450	0.056	0.075
Well 162	0.165	0.200	0.530	0.064	0.088
Well 136	0.130	0.200	0.546	0.064	0.101

Table 5.26: Groundwater Inorganic Analysis in twenty-five (25) Wells at Baruwa (December, 2006)

WELL LOCATION	FERROUS IRON (ppm)	MANGANESE (ppm)	NITRATE (ppm)	SULPHATE (ppm)	DO (ppm)
Well 20	1.892	0.530	0.210	0.017	0.000
Well 10	1.536	0.422	0.210	0.019	0.000
Well 41	0.912	0.361	0.282	0.031	0.000
Well 44	0.844	0.360	0.301	0.033	0.006
Well 42	0.720	0.355	0.323	0.032	0.006
Well 45	0.715	0.362	0.320	0.031	0.007
Well 48	0.722	0.360	0.321	0.031	0.006
Well 73	0.631	0.278	0.339	0.037	0.010
Well 51	0.603	0.252	0.336	0.040	0.010
Well 64	0.575	0.243	0.340	0.040	0.011
Well 75	0.571	0.242	0.352	0.041	0.011
Well 157	0.506	0.240	0.361	0.040	0.017
Well 159	0.483	0.241	0.360	0.040	0.018
Well 14	0.458	0.233	0.365	0.041	0.021
Well 144	0.427	0.230	0.374	0.042	0.028
Well 155	0.412	0.230	0.375	0.041	0.031
Well 143	0.362	0.231	0.378	0.040	0.033
Well 140	0.350	0.230	0.386	0.041	0.032
Well 13	0.314	0.223	0.405	0.045	0.044
Well 14	0.298	0.223	0.410	0.043	0.053
Well 15	0.254	0.220	0.410	0.046	0.053
Well 168	0.218	0.215	0.405	0.048	0.062
Well 139	0.213	0.210	0.411	0.048	0.064
Well 162	0.175	0.202	0.421	0.047	0.078
Well 136	0.170	0.201	0.428	0.056	0.095
DO - DISSOLVED OXYGEN					

```

program SandMain [Laboratory-Scale]
  parameter(ni=140,nj=30,nk=80)
  real*8 c(ni,nj,nk),cin(ni,nj,nk),cn(ni,nj,nk),cb(ni,nj,nk)
  real*8 u(ni,nj,nk),v(ni,nj,nk),w(ni,nj,nk)
  real*8 dfx(ni,nj,nk),dfy(ni,nj,nk),dfz(ni,nj,nk)
  real*8 x(ni),y(nj),z(nk)
  real*8 courX(ni,nj,nk), courY(ni,nj,nk)
  real*8 courZ(ni,nj,nk)
  real*8 rX(ni,nj,nk), rY(ni,nj,nk),rZ(ni,nj,nk)
  real*8 dk(ni,nj,nk)
  real*8 is1(5),is2(5),js1(5),js2(5),ks1(5),ks2(5),
  & scin(5),sctp(5)
  real*8 dx,dy,dz,dt,otm,stm,cfactor
  real*8 dfx0,dfy0,dfz0,rtd,decay,u0,v0,w0,cbkg

  character*15 outfileXY,outfileXZ,outfileYZ
  integer ipout(12),jpout(12),kpout(12)

```

Input Section

```

  open(1,file='in.dat')
  read(1,*) dx,dy,dz
  write(*,*) dx,dy,dx

  read(1,*) u0
  v0 = 0.0e0
  w0 = 0.0e0
  write(*,*) u0,v0,w0

  read(1,*) dfx0,dfy0,dfz0
  write(*,*) dfx0,dfy0,dfz0

  read(1,*) dt,otm,stm
  write(*,*) dt,otm,stm

  read(1,*) iout,jout,kout
  write(*,*) iout,jout,kout

  read(1,*) rtd,decay
  write(*,*) rtd,decay

  read(1,*) cbkg, nsp
  write(*,*) cbkg, nsp

  do is = 1,nsp
    read(1,*) is1(is), is2(is), js1(is), js2(is),
    & ks1(is), ks2(is),scin(is), sctp(is)

```

```

write(*,*) is1(is), is2(is), js1(is), js2(is),
&      ks1(is), ks2(is), scin(is), sctp(is)
scin(is) = scin(is) * 1e-9
enddo

```

```

read(1,*) ntout
do iot=1,ntout
  read(1,*) ipout(iot),jpout(iot),kpout(iot)
  write(*,*) ipout(iot),jpout(iot),kpout(iot)
enddo
close(1)

```

Compute important some parameters

```

stm = stm*3600.
otm = otm*3600.
dt = dt*60.
ntime_stop = stm/dt
ntime_output = otm/dt
decay = decay/86400.0

```

```

cfactor = 2.5e6

```

```

cbkg = cbkg/cfactor

```

```

do i=1,ni
  x(i) = (i-1)*dx
enddo

```

```

do j=1,nj
  y(j) = (j-1)*dy
enddo

```

```

do k=1,nk
  z(k) = (k-1)*dz
enddo

```

```

do i=1,ni
  do j=1,nj
    do k=1,nk
      u(i,j,k) = u0/rtd
      v(i,j,k) = v0/rtd
      w(i,j,k) = w0/rtd
      dfx(i,j,k) = dfx0/rtd
      dfy(i,j,k) = dfy0/rtd
      dfz(i,j,k) = dfz0/rtd
    enddo
  enddo
enddo

```

```

courX(i,j,k) = u(i,j,k)*dt/dx
courY(i,j,k) = v(i,j,k)*dt/dy
courZ(i,j,k) = w(i,j,k)*dt/dz

```

```

rX(i,j,k) = dfx(i,j,k)*dt/dx**2
rY(i,j,k) = dfy(i,j,k)*dt/dy**2
rZ(i,j,k) = dfz(i,j,k)*dt/dz**2

```

```

c(i,j,k) = cbkg
cin(i,j,k) = 0.0

```

```

do is = 1,nsp
  if(i >= is1(is) .and. i <= is2(is)) then
    if(j >= js1(is) .and. j <= js2(is)) then
      if(k >= ks1(is) .and. k <= ks2(is)) then
        cin(i,j,k) = scin(is)
        c(i,j,k) = cin(i,j,k) + c(i,j,k)
      endif
    endif
  endif
enddo
enddo
enddo
enddo

```

Output at time = 0

```

ikt = 0
ikot = 0
TimeNow = 0.
open(4,file='TimeConc.dat')
write(4,12) TimeNow/3600.0,
&      (c(iout,jout,kout)*cfactor,iot=1,ntout)
call flush(4)

```

```

open(2,file='Res000.dat')
do j=1,nj
  write(2,12)(c(i,j,kout)*cfactor, i=1,ni)
enddo
close(2)

```

DO it = 1,ntime_stop

TimeNow = it*dt

```

do i=1,ni
  do j=1,nj
    do k=1,nk
      cb(i,j,k) = cn(i,j,k)
    enddo
  enddo
enddo

```

```

if (it.eq.1) then
  call UpstreamAdv(c,courX,courY,courZ,dk,ni,nj,nk)
  cb(i,j,k) = cn(i,j,k)
  dt2 = dt
else

```



```
call LeapFrogAdv(c,courX,courY,courZ,dk,ni,nj,nk)
```

```
dt2 = dt*2
```

```
endif
```

```
call DispersionAScheme(c,rX,rY,rZ,dk,ni,nj,nk)
```

```
do i=1,ni
```

```
do j=1,nj
```

```
do k=1,nk
```

```
cn(i,j,k) = cn(i,j,k) + dk(i,j,k) + cin(i,j,k)*dt
```

```
& + decay*cn(i,j,k)*dt
```

```
enddo
```

```
enddo
```

```
enddo
```

```
Check the continuity of the source
```

```
do i=1,ni
```

```
do j=1,nj
```

```
do k=1,nk
```

```
do is = 1,nsp
```

```
if(i>= is1(is) .and. i<=is2(is)) then
```

```
if(j >= js1(is) .and. j<=js2(is)) then
```

```
if(k >= ks1(is) .and. k<=ks2(is)) then
```

```
if(TimeNow >= sctp(is)) cin(i,j,k) = 0.0
```

```
endif
```

```
endif
```

```
endif
```

```
enddo
```

```
enddo
```

```
enddo
```

```
enddo
```

```
write(*,*) 'Time: ',TimeNow/3600.0, ' itr: ',it, ' of',ntime_stop
```

```
Output at the right time
```

```
ikot = ikot + 1
```

```
ntime_ut = 10*60/dt
```

```
if (ikot .eq. ntime_ut) then
```

```
write(4,12) TimeNow/3600.0,
```

```
& (c(ipout(iot),jpout(iot),kpout(iot))*cfactor,iot=1,ntout)
```

```
call flush(4)
```

```
ikot=0
```

```
endif
```

```
ikt = ikt + 1
```

```
if (ikt .eq. ntime_output) then
```

```
ifile = ifile + 1
```

```
if (ifile<10) then
```

```
write(outfileXY,5)ifile
```

```
write(outfileXZ,6)ifile
```

```

        write(outfileYZ,7)ifile
elseif(ifile<100) then
    write(outfileXY,15)ifile
    write(outfileXZ,16)ifile
    write(outfileYZ,17)ifile
elseif(ifile<1000) then
    write(outfileXY,25)ifile
    write(outfileXZ,26)ifile
    write(outfileYZ,27)ifile
else
    stop 'too many output files'
endif

5   format('XYRes00',i1,'.dat')
6   format('XZRes00',i1,'.dat')
7   format('YZRes00',i1,'.dat')

15  format('XYRes0' ,i2,'.dat')
16  format('XZRes0' ,i2,'.dat')
17  format('YZRes0' ,i2,'.dat')

25  format('XYRes'  ,i3,'.dat')
26  format('XZRes'  ,i3,'.dat')
27  format('YZRes'  ,i3,'.dat')

open(2,file=outfileXY)
do j=1,nj
    write(2,12)(c(i,j,kout)*cfactor, i=1,ni)
enddo
close(2)

open(2,file=outfileXZ)
do k=1,nk
    write(2,12)(c(i,jout,k)*cfactor, i=1,ni)
enddo
close(2)

open(2,file=outfileYZ)
do k=1,nk
    write(2,12)(c(iout,j,k)*cfactor, j=1,nj)
enddo
close(2)

ikt = 0

endif

ENDDO
close(4)

12  format(200(1x,f7.2))
end

```

Subroutine UpstreamScheme Advection(var,courX,courY,courZ,dk, ni,nj,nk)

real*8 var(ni,nj,nk),dk(ni,nj,nk)

real*8 courX(ni,nj,nk), courY(ni,nj,nk),courZ(ni,nj,nk)

real nu,pu

do i=1,ni

do j=1,nj

do k=1,nk

----- Along X

ip1=i+1

im1=i-1

io = sign(1.0, courX(i,j,k))

pu = abs(0.5*(io+1))

nu = abs(0.5*(io-1))

if(ip1>ni) ip1 = ni

if(im1<1) im1 = 1

dvarp = pu*(var(i,j,k) - var(im1,j,k))

dvarn = nu*(var(ip1,j,k) - var(i,j,k))

dk(i,j,k) = dk(i,j,k) - courX(i,j,k)*(dvarp + dvarn)

----- Along Y

jp1=j+1

jml=j-1

if(jp1>nj) jp1 = nj

if(jml<1) jml = 1

io = sign(1.0, courY(i,j,k))

pu = abs(0.5*(io+1))

nu = abs(0.5*(io-1))

dvarp = pu*(var(i,j,k) - var(i,jml,k))

dvarn = nu*(var(i,jp1,k) - var(i,j,k))

dk(i,j,k) = dk(i,j,k) - courY(i,j,k)*(dvarp + dvarn)

----- Along Z

kp1=k+1

kml=k-1

if(kp1>nk) kp1 = nk

if(kml<1) kml = 1

io = sign(1.0, courZ(i,j,k))

pu = abs(0.5*(io+1))

nu = abs(0.5*(io-1))

dvarp = pu*(var(i,j,k) - var(i,j,kml))

dvarn = nu*(var(i,j,kp1) - var(i,j,k))

dk(i,j,k) = dk(i,j,k) - courZ(i,j,k)*(dvarp + dvarn)

enddo

enddo

enddo

```

end
Subroutine DispersionAScheme(var,rX,rY,rZ,dk,ni,nj,nk)
  real*8 var(ni,nj,nk),dk(ni,nj,nk)
  real*8 rX(ni,nj,nk), rY(ni,nj,nk),rZ(ni,nj,nk)

  do i=1,ni
    do j=1,nj
      do k=1,nk

!----- Along X
        ip1=i+1
        im1=i-1
        if(ip1>ni) ip1 = ni
        if(im1<1) im1 = 1

        diff = var(im1,j,k) -2.0*var(i,j,k) + var(ip1,j,k)
        dk(i,j,k) = dk(i,j,k) +rX(i,j,k)*diff

!----- Along Y
        jp1=j+1
        jm1=j-1
        if(jp1>nj) jp1 = nj
        if(jm1<1) jm1 = 1

        diff = var(i,jm1,k) -2.0*var(i,j,k) + var(i,jp1,k)
        dk(i,j,k) = dk(i,j,k) +rY(i,j,k)*diff

!----- Along Z
        kp1=k+1
        km1=k-1
        if(kp1>nk) kp1 = nk
        if(km1<1) km1 = 1

        diff = var(i,j,km1) -2.0*var(i,j,k) + var(i,j,kp1)
        dk(i,j,k) = dk(i,j,k) +rZ(i,j,k)*diff

      enddo
    enddo
  enddo

end

```

```

program SandMain [Field-Scale]
  parameter(ni=30,nj=35,nk=10)
  real*8 c(ni,nj,nk),cin(ni,nj,nk),cn(ni,nj,nk),cb(ni,nj,nk)
  real*8 u(ni,nj,nk),v(ni,nj,nk),w(ni,nj,nk)
  real*8 dfx(ni,nj,nk),dfy(ni,nj,nk),dfz(ni,nj,nk)
  real*8 x(ni),y(nj),z(nk)
  real*8 courX(ni,nj,nk), courY(ni,nj,nk)
  real*8 courZ(ni,nj,nk)
  real*8 rX(ni,nj,nk), rY(ni,nj,nk),rZ(ni,nj,nk)
  real*8 dk(ni,nj,nk)
  real*8 is1(5),is2(5),js1(5),js2(5),ks1(5),ks2(5),
  &      scin(5),sctp(5)
  real*8 dx,dy,dz,dt,otm,stm,cfactor
  real*8 dfx0,dfy0,dfz0,rtd,decay,u0,v0,w0,cbkg

  character*15 outfileXY,outfileXZ,outfileYZ
  integer ipout(12),jpout(12),kpout(12)

```

Input Section

```

  open(1,file='in.dat')
  read(1,*) dx,dy,dz
  write(*,*) dx,dy,dx

  read(1,*) u0
  v0 = 0.0e0
  w0  = 0.0e0
  write(*,*) u0,v0,w0

  read(1,*) dfx0,dfy0,dfz0
  write(*,*) dfx0,dfy0,dfz0

  read(1,*) dt,otm,stm
  write(*,*) dt,otm,stm

  read(1,*) iout,jout,kout
  write(*,*) iout,jout,kout

  read(1,*) rtd,decay
  write(*,*) rtd,decay

  read(1,*) cbkg,nsp
  write(*,*) cbkg,nsp

  do is = 1,nsp
    read(1,*) is1(is), is2(is), js1(is), js2(is),
    &      ks1(is), ks2(is),scin(is), sctp(is)

    write(*,*) is1(is), is2(is), js1(is), js2(is),
    &      ks1(is), ks2(is),scin(is), sctp(is)
  enddo

```

```
scin(is) = scin(is) * 1e-9
enddo
```

```
read(1,*) ntout
do iot=1,ntout
  read(1,*) ipout(iot),jpout(iot),kpout(iot)
  write(*,*) ipout(iot),jpout(iot),kpout(iot)
enddo
```

```
close(1)
```

Compute important some parameters

```
stm = stm*3600.
otm = otm*3600.
dt = dt*60.
ntime_stop = stm/dt
ntime_output = otm/dt
decay = decay/86400.0
```

```
cfactor = 2.5e6
```

```
cbkg = cbkg/cfactor
```

```
do i=1,ni
  x(i) = (i-1)*dx
enddo
```

```
do j=1,nj
  y(j) = (j-1)*dy
enddo
```

```
do k=1,nk
  z(k) = (k-1)*dz
enddo
```

```
do i=1,ni
  do j=1,nj
    do k=1,nk
      u(i,j,k) = u0/rtd
      v(i,j,k) = v0/rtd
      w(i,j,k) = w0/rtd
      dfx(i,j,k) = dfx0/rtd
      dfy(i,j,k) = dfy0/rtd
      dfz(i,j,k) = dfz0/rtd
```

```
courX(i,j,k) = u(i,j,k)*dt/dx
courY(i,j,k) = v(i,j,k)*dt/dy
courZ(i,j,k) = w(i,j,k)*dt/dz
```

```
rX(i,j,k) = dfx(i,j,k)*dt/dx**2
rY(i,j,k) = dfy(i,j,k)*dt/dy**2
```

```
rZ(i,j,k) = dfz(i,j,k)*dt/dz**2
```

```
c(i,j,k) = cbkg
```

```
cin(i,j,k) = 0.0
```

```
do is = 1,nsp
```

```
  if(i>= is1(is) .and. i<=is2(is)) then
```

```
    if(j >= js1(is) .and. j<=js2(is)) then
```

```
      if(k >= ks1(is) .and. k<=ks2(is)) then
```

```
        cin(i,j,k) = scin(is)
```

```
        c(i,j,k) = cin(i,j,k) + c(i,j,k)
```

```
      endif
```

```
    endif
```

```
  endif
```

```
enddo
```

```
  enddo
```

```
  enddo
```

```
enddo
```

Output at time = 0

```
ikt = 0
```

```
ikot = 0
```

```
TimeNow = 0.
```

```
open(4,file='TimeConc.dat')
```

```
write(4,12) TimeNow/3600.0,
```

```
&      (c(iout,jout,kout)*cfactor,iot=1,ntout)
```

```
call flush(4)
```

```
open(2,file='Res000.dat')
```

```
do j=1,nj
```

```
  write(2,12)(c(i,j,kout)*cfactor, i=1,ni)
```

```
enddo
```

```
close(2)
```

```
DO it = 1,ntime_stop
```

```
TimeNow = it*dt
```

```
  do i=1,ni
```

```
    do j=1,nj
```

```
      do k=1,nk
```

```
        cb(i,j,k) = cn(i,j,k)
```

```
cn(i,j,k) = c(i,j,k)
```

```
dk(i,j,k) = 0.0
```

```
enddo
```

```
  enddo
```

```
enddo
```

```
if (it.eq.1) then
```

```
  call UpstreamAdv(c,courX,courY,courZ,dk,ni,nj,nk)
```

```
  cb(i,j,k) = cn(i,j,k)
```

```
  dt2 = dt
```

```

else
  call LeapFrogAdv(c,courX,courY,courZ,dk,ni,nj,nk)
  dt2 = dt*2
endif

```

```

call DispersionAScheme(c,rX,rY,rZ,dk,ni,nj,nk)

```

```

do i=1,ni
  do j=1,nj
    do k=1,nk
      c(i,j,k) = cn(i,j,k) + dk(i,j,k) + cin(i,j,k)*dt
      &          + decay*cn(i,j,k)*dt
    enddo
  enddo
enddo

```

===== Check the continuity of the source

```

do i=1,ni
  do j=1,nj
    do k=1,nk

      do is = 1,nsp
        if(i>= is1(is) .and. i<=is2(is)) then
          if(j >= js1(is) .and. j<=js2(is)) then
            if(k >= ks1(is) .and. k<=ks2(is)) then
              if(TimeNow >= sctp(is)) cin(i,j,k) = 0.0
            endif
          endif
        endif
      enddo
    enddo
  enddo
enddo

```

```

enddo
enddo
enddo

```

```

write(*,*) 'Time: ',TimeNow/3600.0, ' itr: ',it, ' of',ntime_stop

```

===== Output at the right time

```

ikot = ikot + 1
ntime_ut = 10*60/dt
if (ikot .eq. ntime_ut) then
  write(4,12) TimeNow/3600.0,
  & (c(ipout(iot),jpout(iot),kpout(iot))*cfactor,iot=1,ntout)
  call flush(4)
  ikot=0
endif
ikt = ikt + 1
if (ikt .eq. ntime_output) then
  ifile = ifile + 1
  if (ifile<10) then
    write(outfileXY,5)ifile

```

```

    write(outfileXZ,6)ifile
    write(outfileYZ,7)ifile
elseif(ifile<100) then
    write(outfileXY,15)ifile
    write(outfileXZ,16)ifile
    write(outfileYZ,17)ifile
elseif(ifile<1000) then
    write(outfileXY,25)ifile
    write(outfileXZ,26)ifile
    write(outfileYZ,27)ifile
else
    stop 'too many output files'
endif

5   format('XYRes00',i1,'.dat')
6   format('XZRes00',i1,'.dat')
7   format('YZRes00',i1,'.dat')

15  format('XYRes0' ,i2,'.dat')
16  format('XZRes0' ,i2,'.dat')
17  format('YZRes0' ,i2,'.dat')

25  format('XYRes' ,i3,'.dat')
26  format('XZRes' ,i3,'.dat')
27  format('YZRes' ,i3,'.dat')

open(2,file=outfileXY)
    do j=1,nj
        write(2,12)(c(i,j,kout)*cfactor, i=1,ni)
    enddo
close(2)

open(2,file=outfileXZ)
    do k=1,nk
        write(2,12)(c(i,jout,k)*cfactor, i=1,ni)
    enddo
close(2)

open(2,file=outfileYZ)
    do k=1,nk
        write(2,12)(c(iout,j,k)*cfactor, j=1,nj)
    enddo
close(2)

    ikt = 0

endif

ENDDDO
close(4)
12  format(200(1x,f7.2))
end
!
```

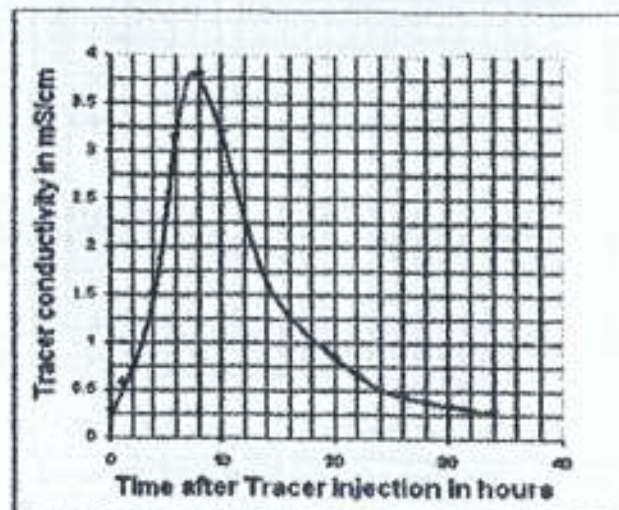


Figure 4: TBC for observation well (OW₂₇) [Port 1]

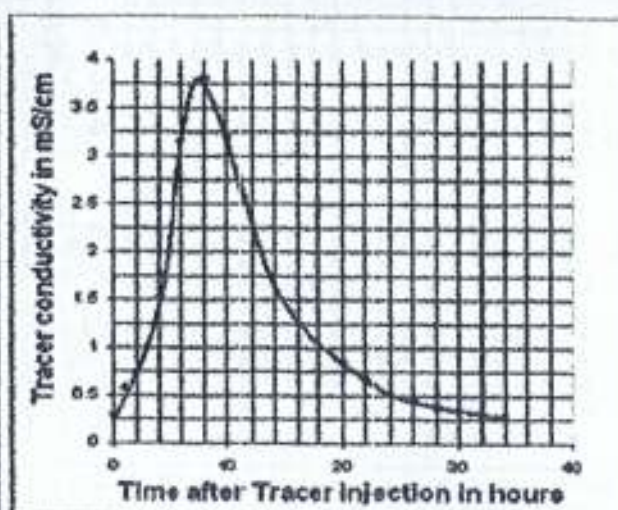


Figure 5: TBC for observation well (OW₂₂) [Port 1]

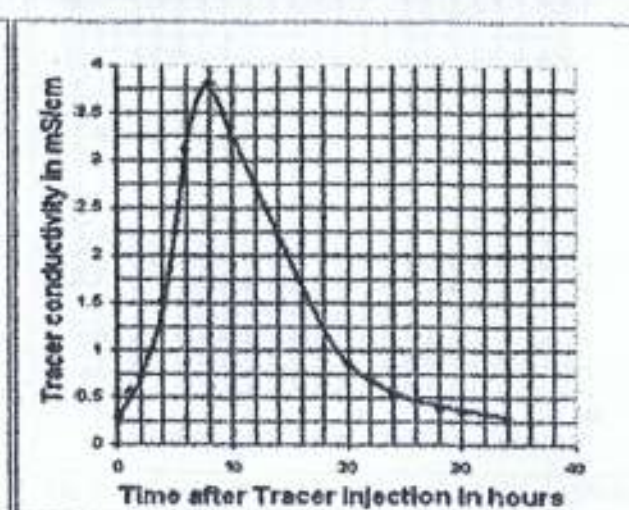


Figure 6: TBC for observation well (OW₁₈) [Port 1]

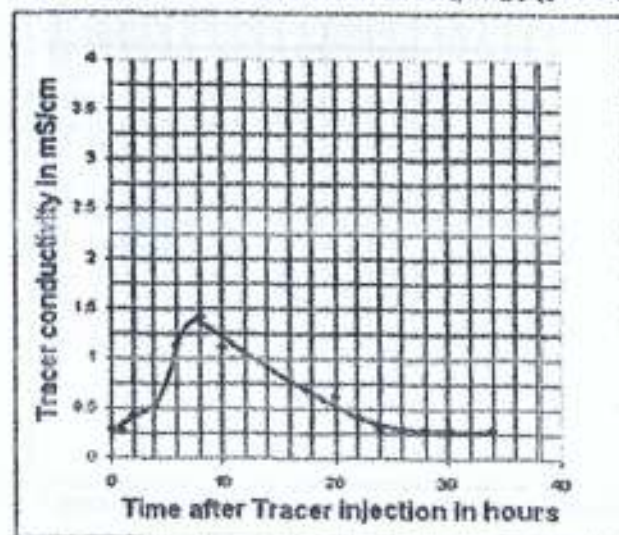


Figure 7: TBC for observation well (OW₀₇) [Port 1]

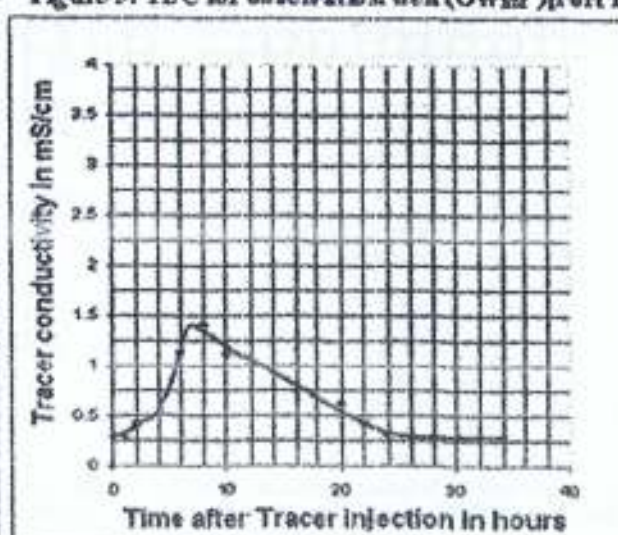


Figure 8: TBC for observation well (OW₀₁) [Port 1]

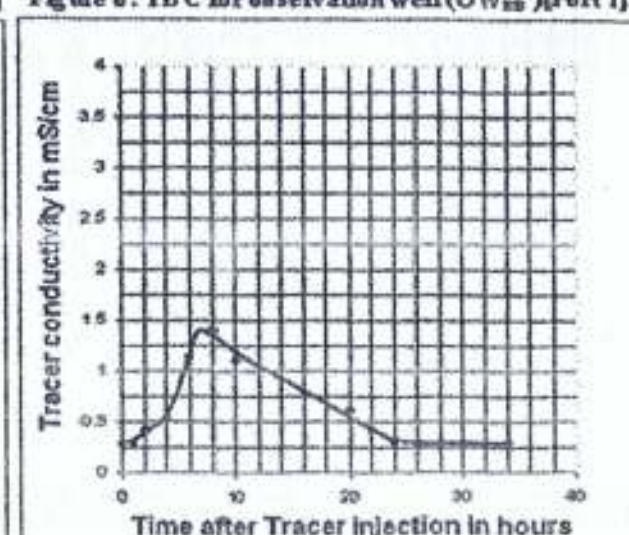


Figure 9: TBC for observation well (OW₀₆) [Port 1]

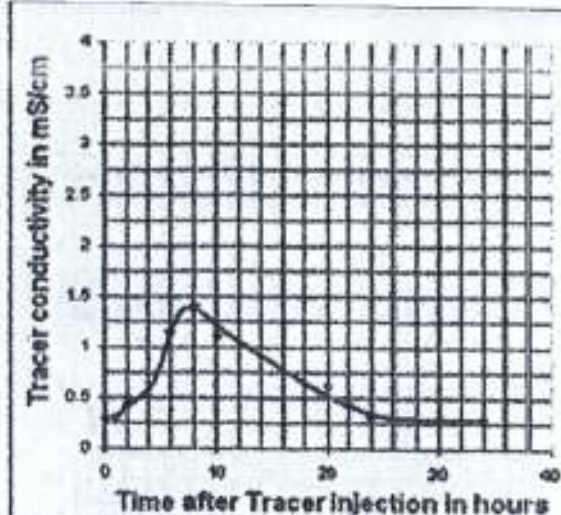


Figure 10: TBC for observation well (OW₂₇) [Port 1]

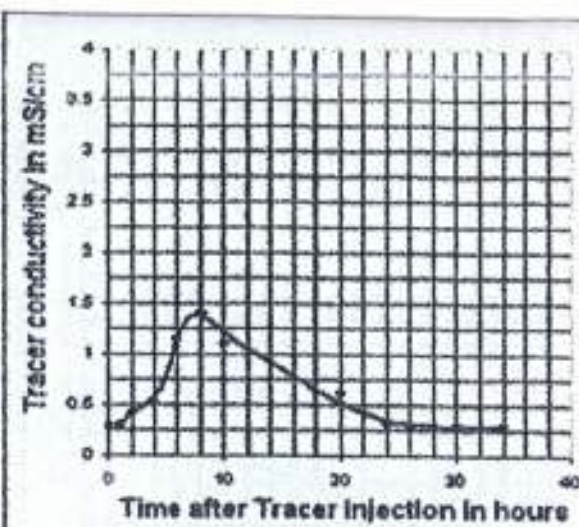


Figure 11: TBC for observation well (OW₂₈) [Port 1]

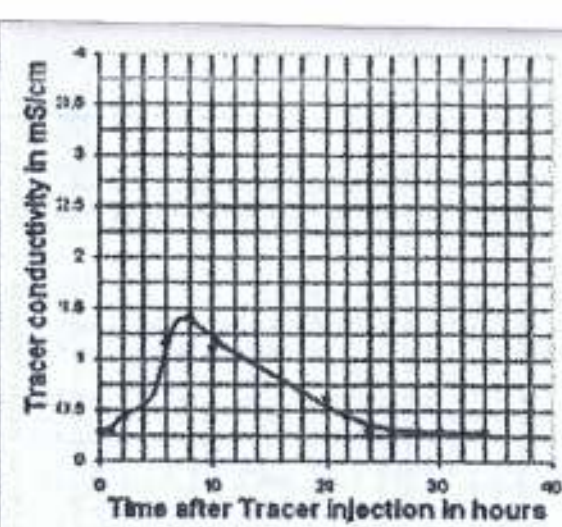


Figure 12: TBC for observation well (OW₂₉) [Port 1]

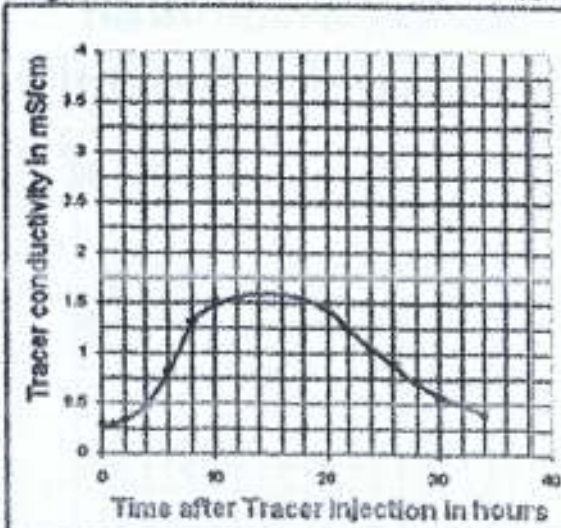


Figure 13: TBC for observation well (OW₃₀) [Port 1]

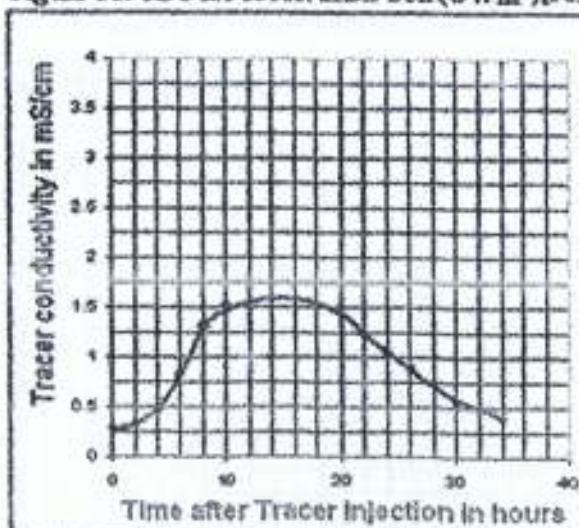


Figure 14: TBC for observation well (OW₃₁) [Port 1]

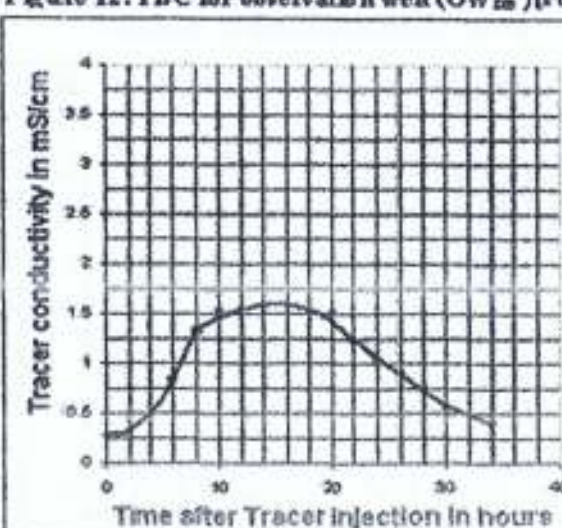


Figure 15: TBC for observation well (OW₃₂) [Port 1]

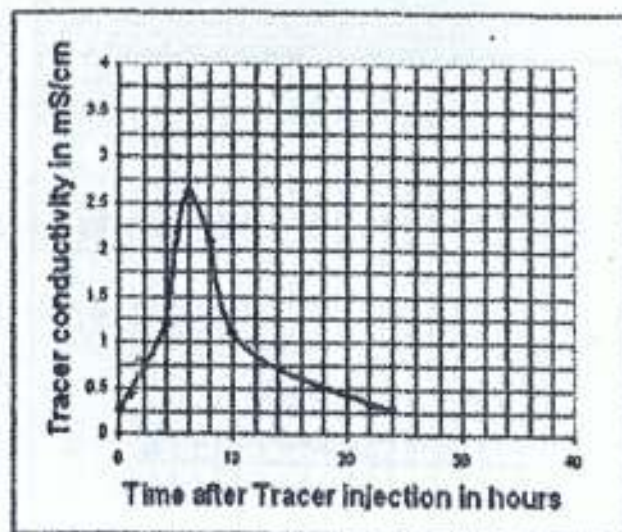


Figure 16: TBC for observation well (OW_{DV}) [Port 2]

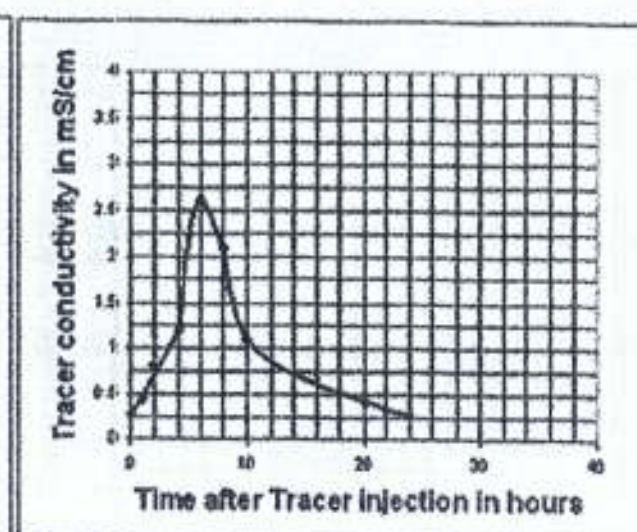


Figure 17: TBC for observation well (OW_{ZSE}) [Port 2]

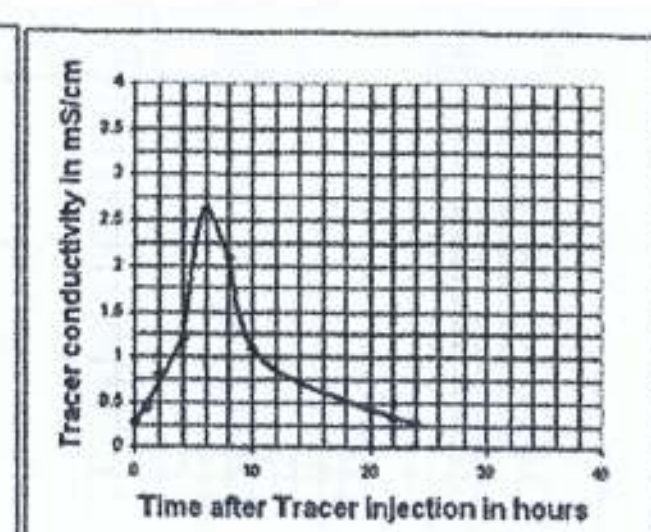


Figure 18: TBC for observation well (OW_{ZM}) [Port 2]

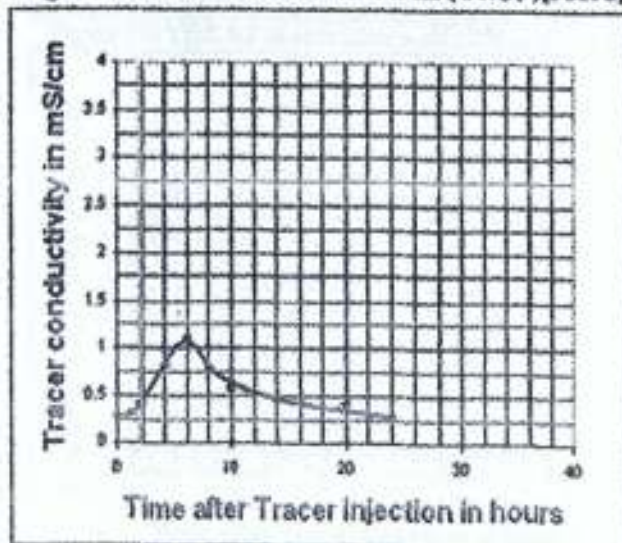


Figure 19: TBC for observation well (OW_{OT}) [Port 2]

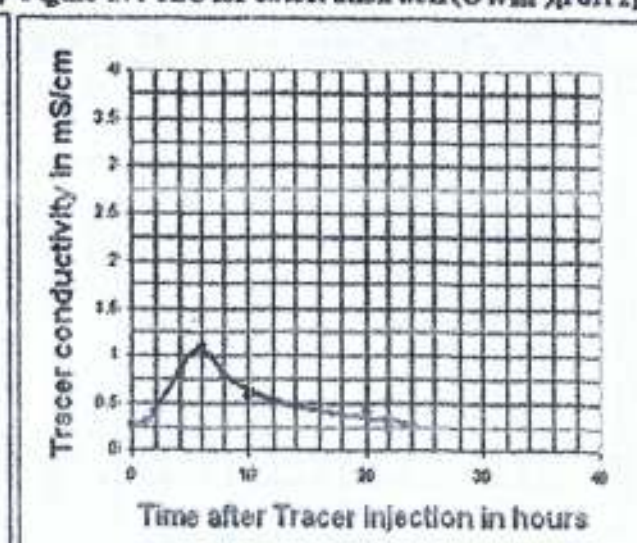


Figure 20: TBC for observation well (OW_{CM}) [Port 2]

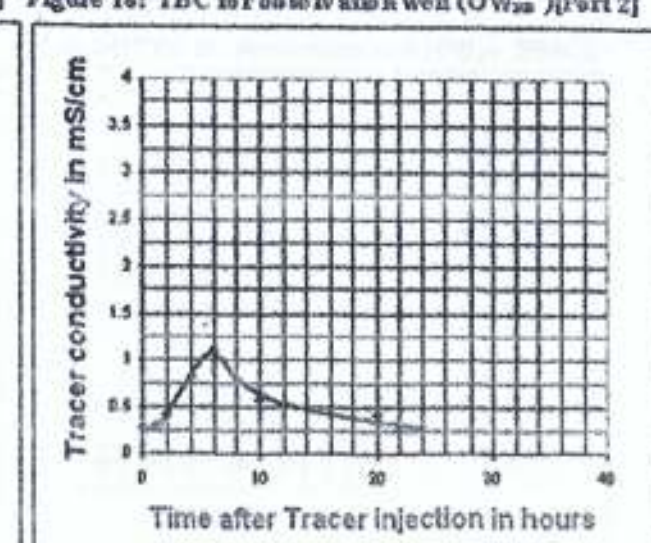


Figure 21: TBC for observation well (OW_{CB}) [Port 2]

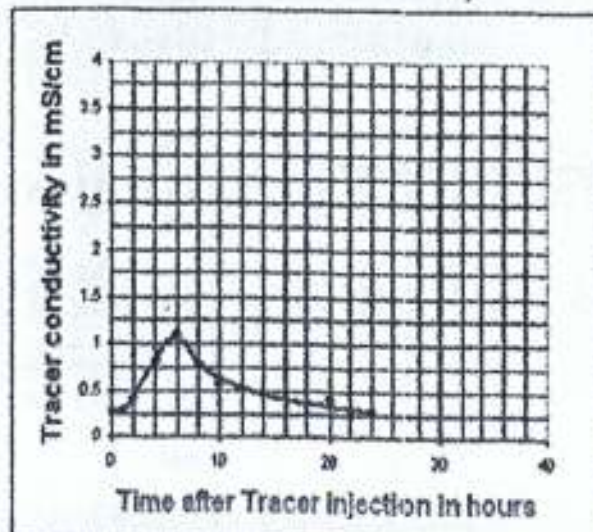


Figure 22: TBC for observation well (OW_{DT}) [Port 2]

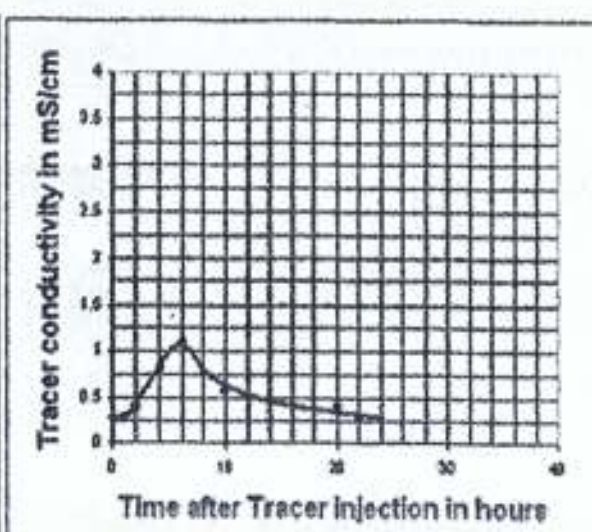


Figure 23: TBC for observation well (OW_{DM}) [Port 2]

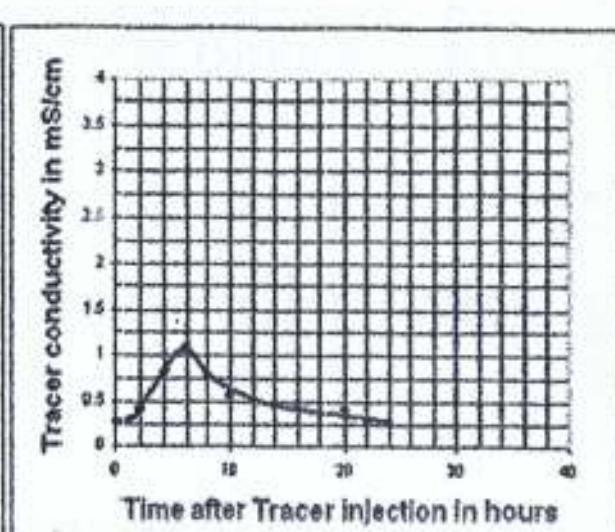


Figure 24: TBC for observation well (OW_{DG}) [Port 2]

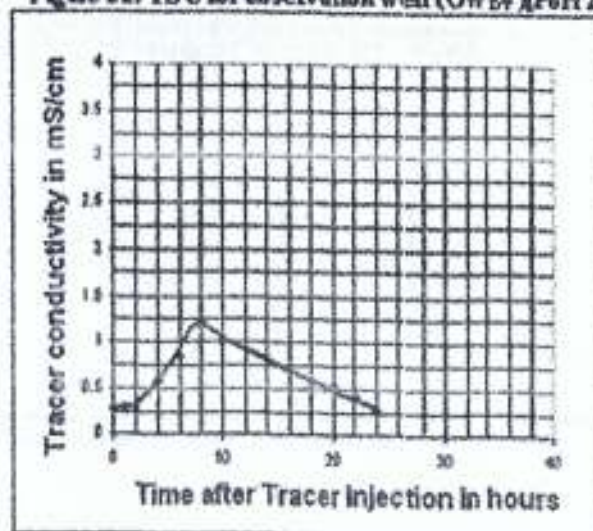


Figure 25: TBC for observation well (OW_{KT}) [Port 2]

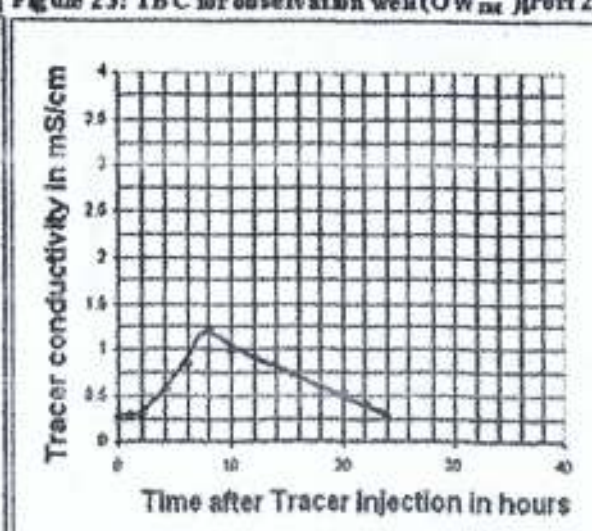


Figure 26: TBC for observation well (OW_{KL}) [Port 2]

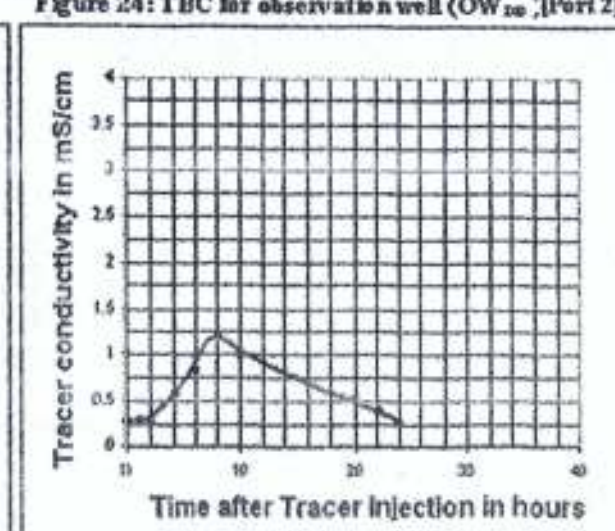
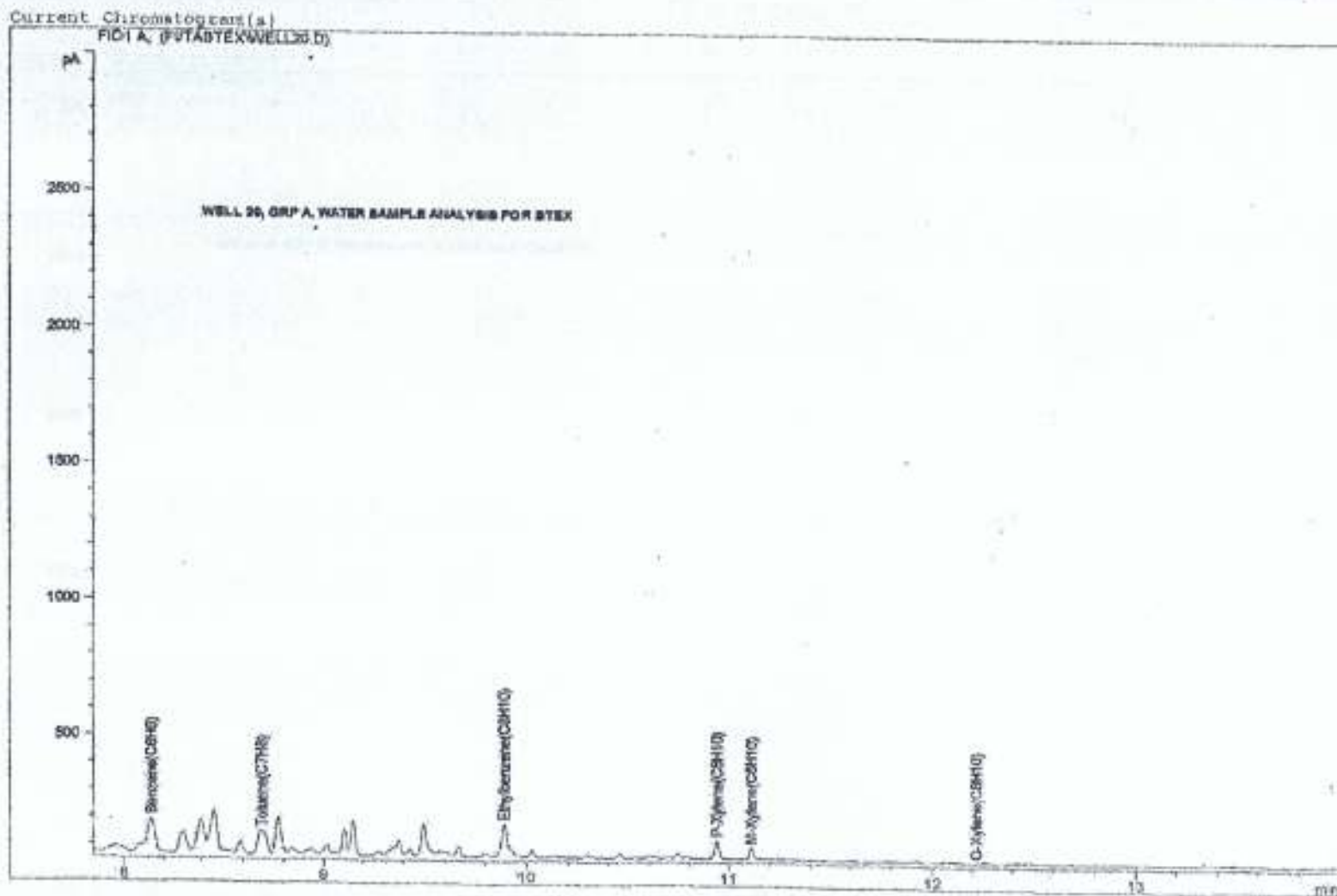


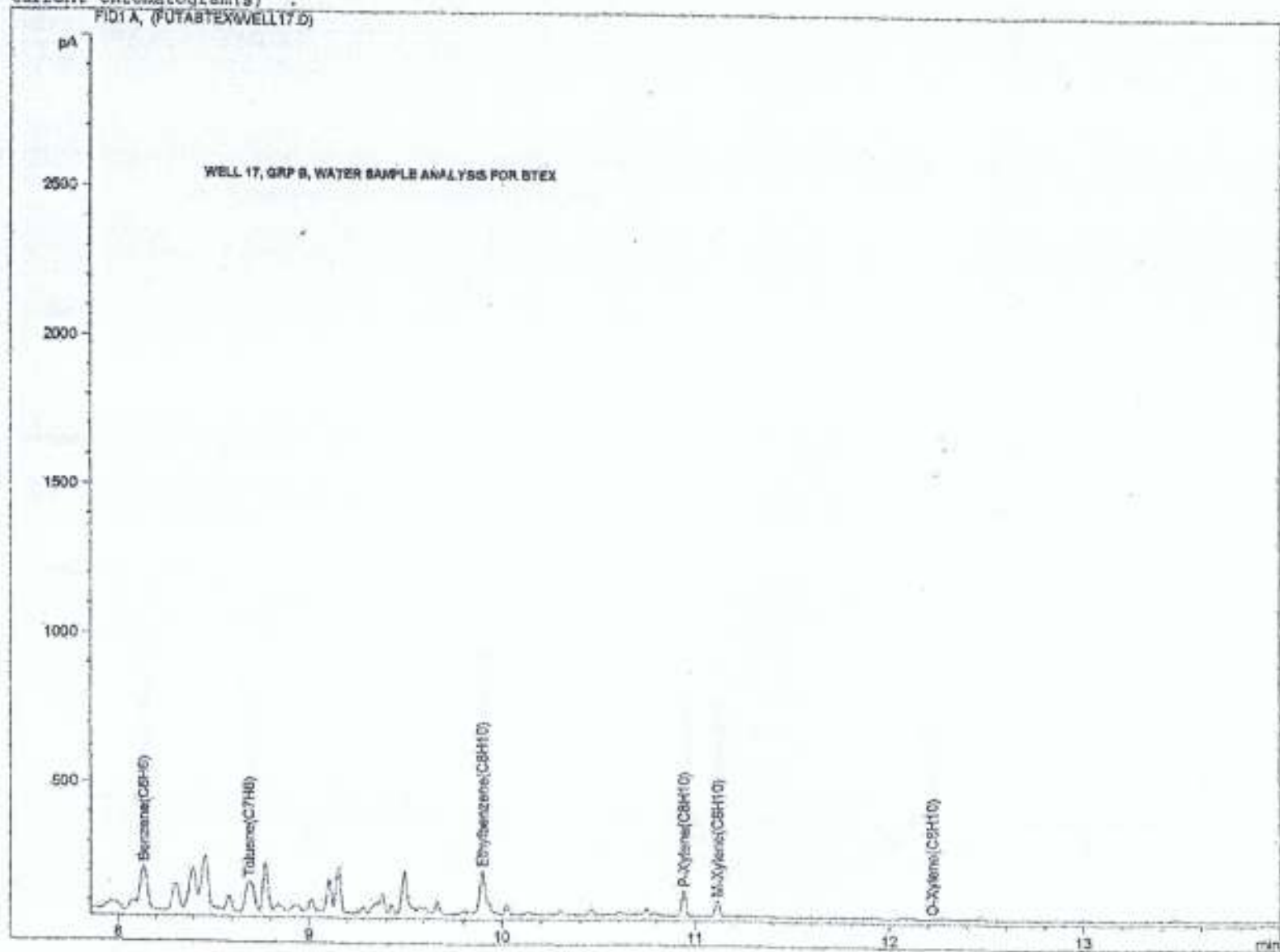
Figure 27: TBC for observation well (OW_{KS}) [Port 2]

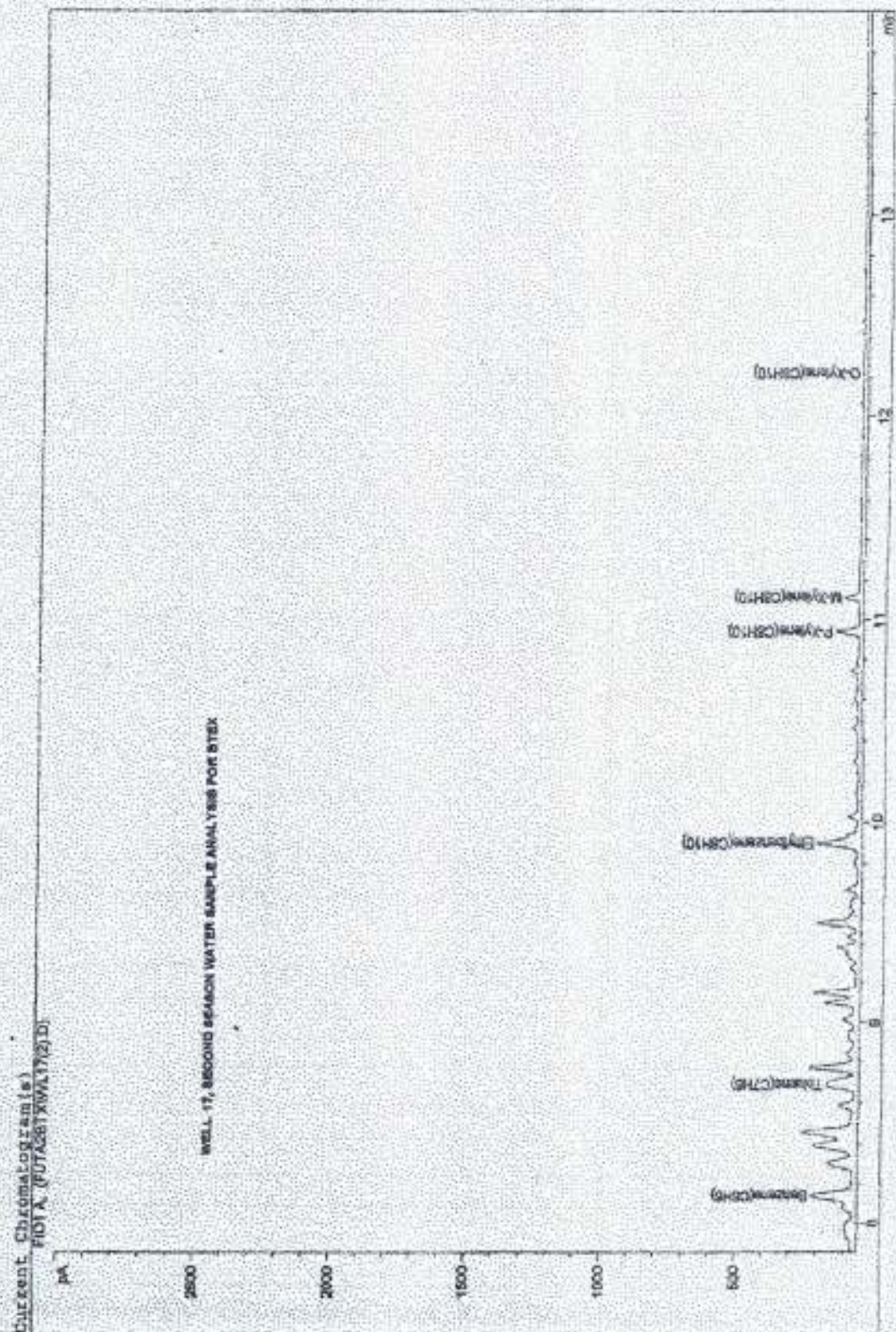


Instrument 1 3/4/2008 1:46:18 AM

Page 1 of 1

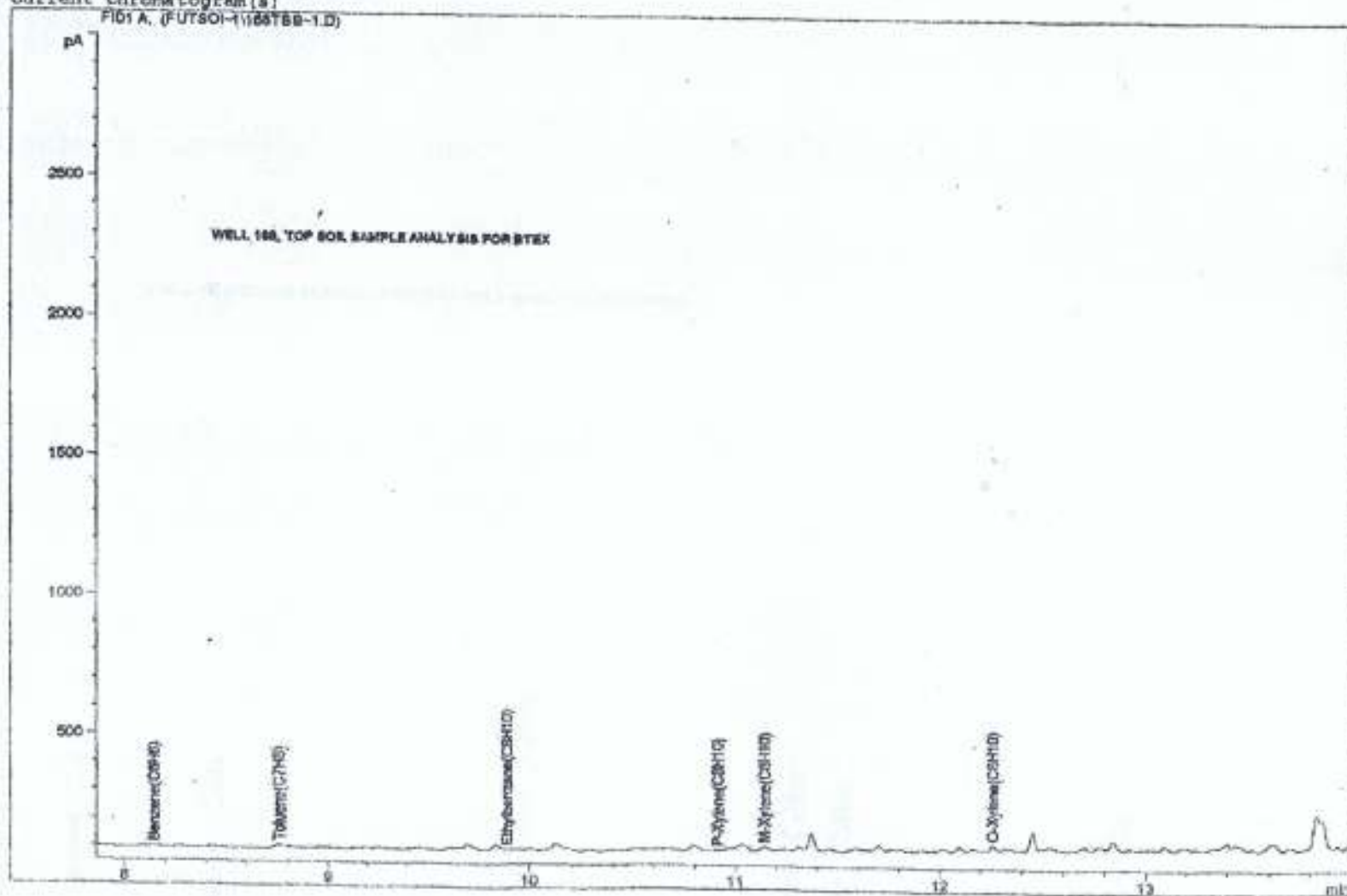
Current Chromatogram(s)





Current Chromatogram(s)

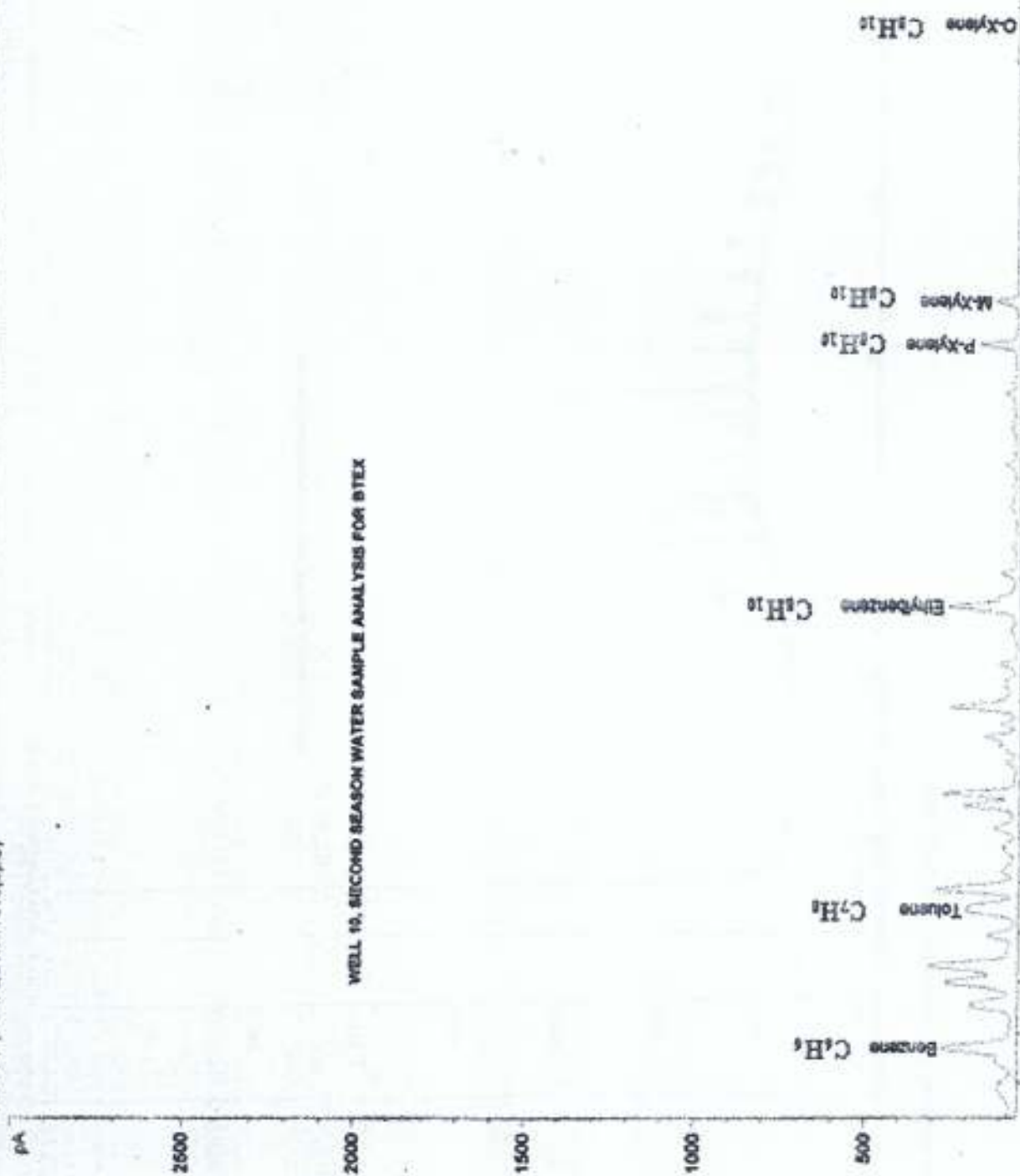
FID1 A, (FUTSOI-1\155TBB-1.D)

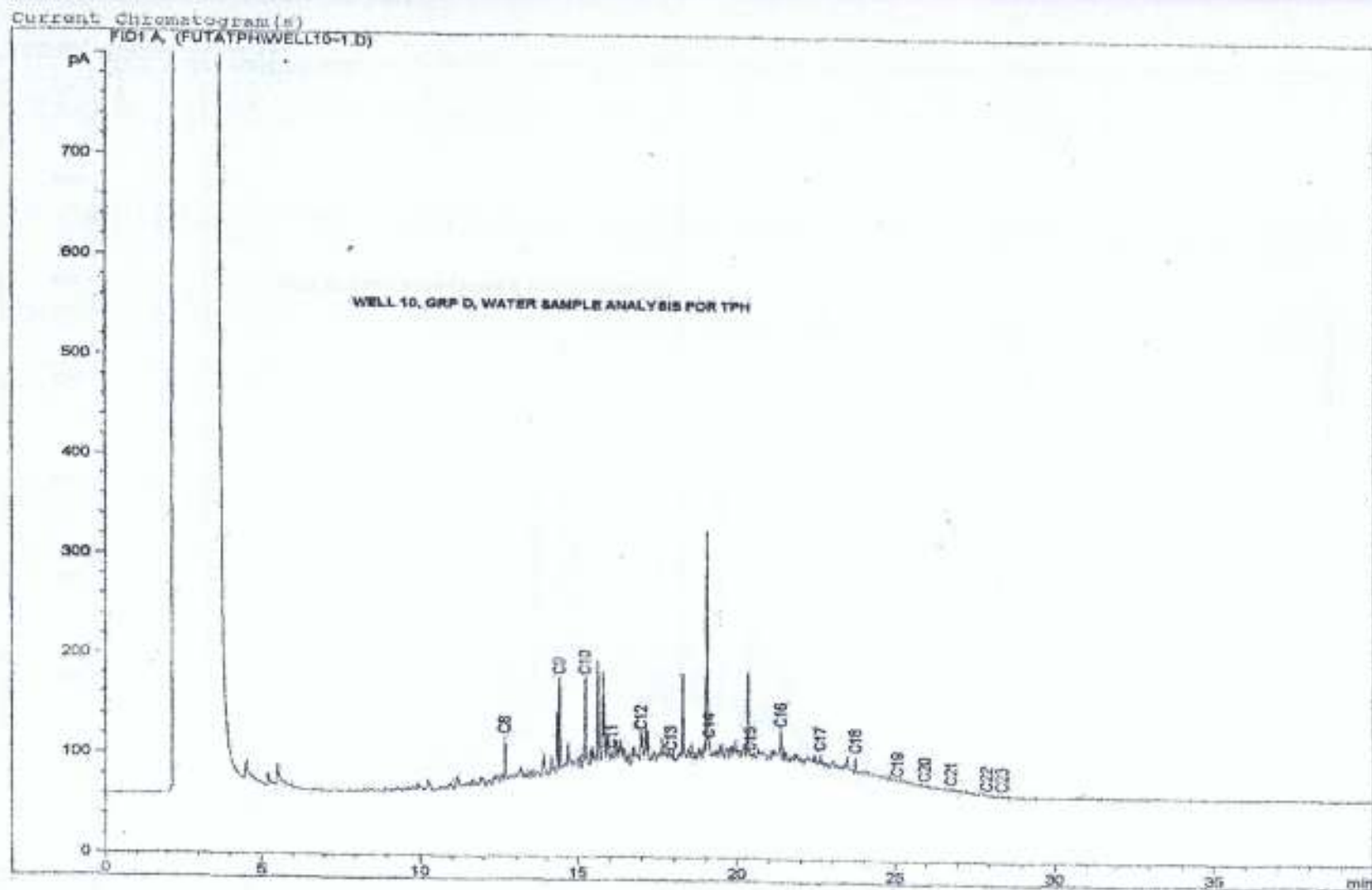


Instrument 1 3/4/2008 1:56:49 AM

Page 1 of 1

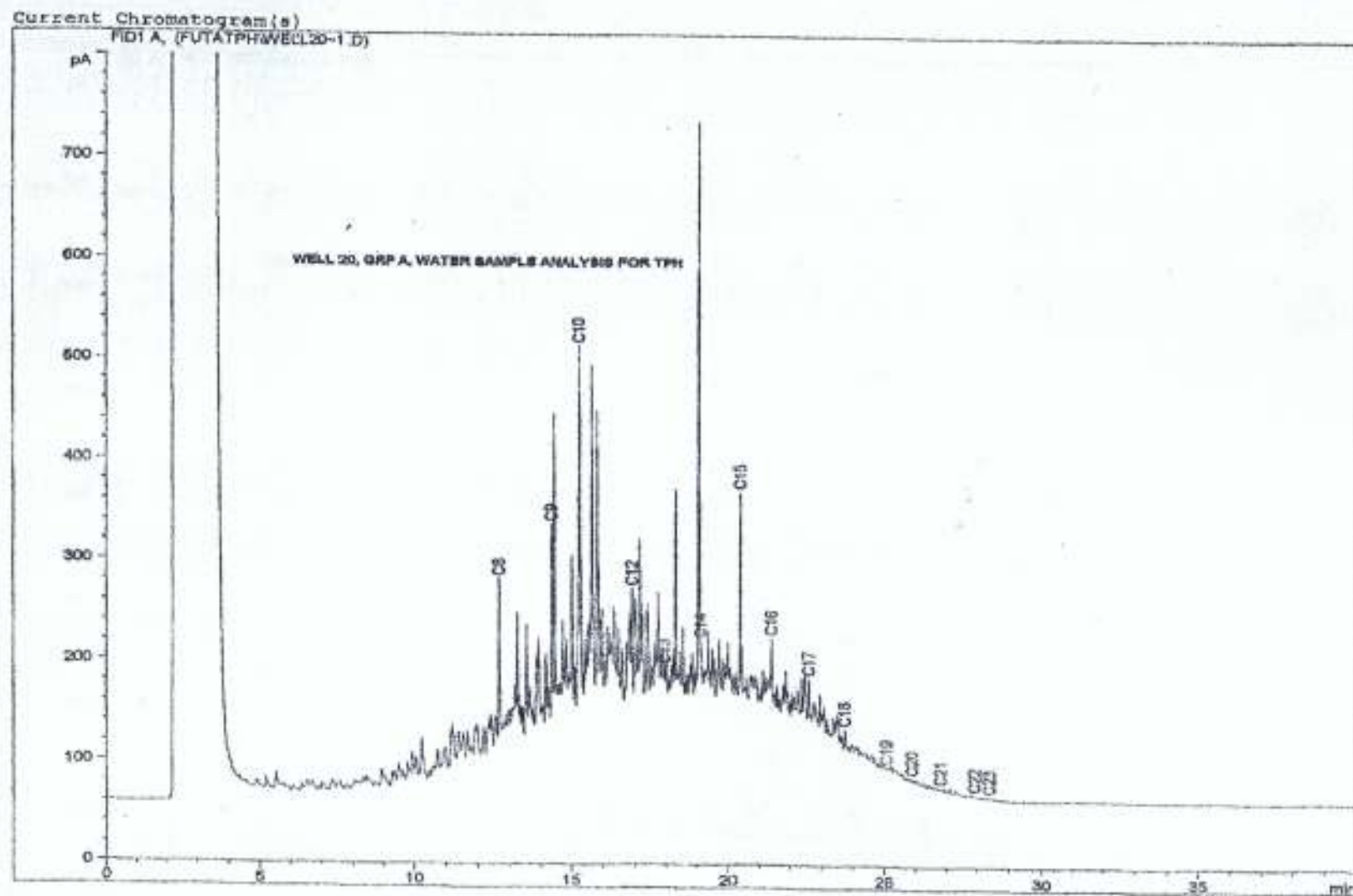
WELL 10, SECOND SEASON WATER SAMPLE ANALYSIS FOR BTEX





Instrument 1 3/4/2008 1:21:35 AM

Page 1 of 1



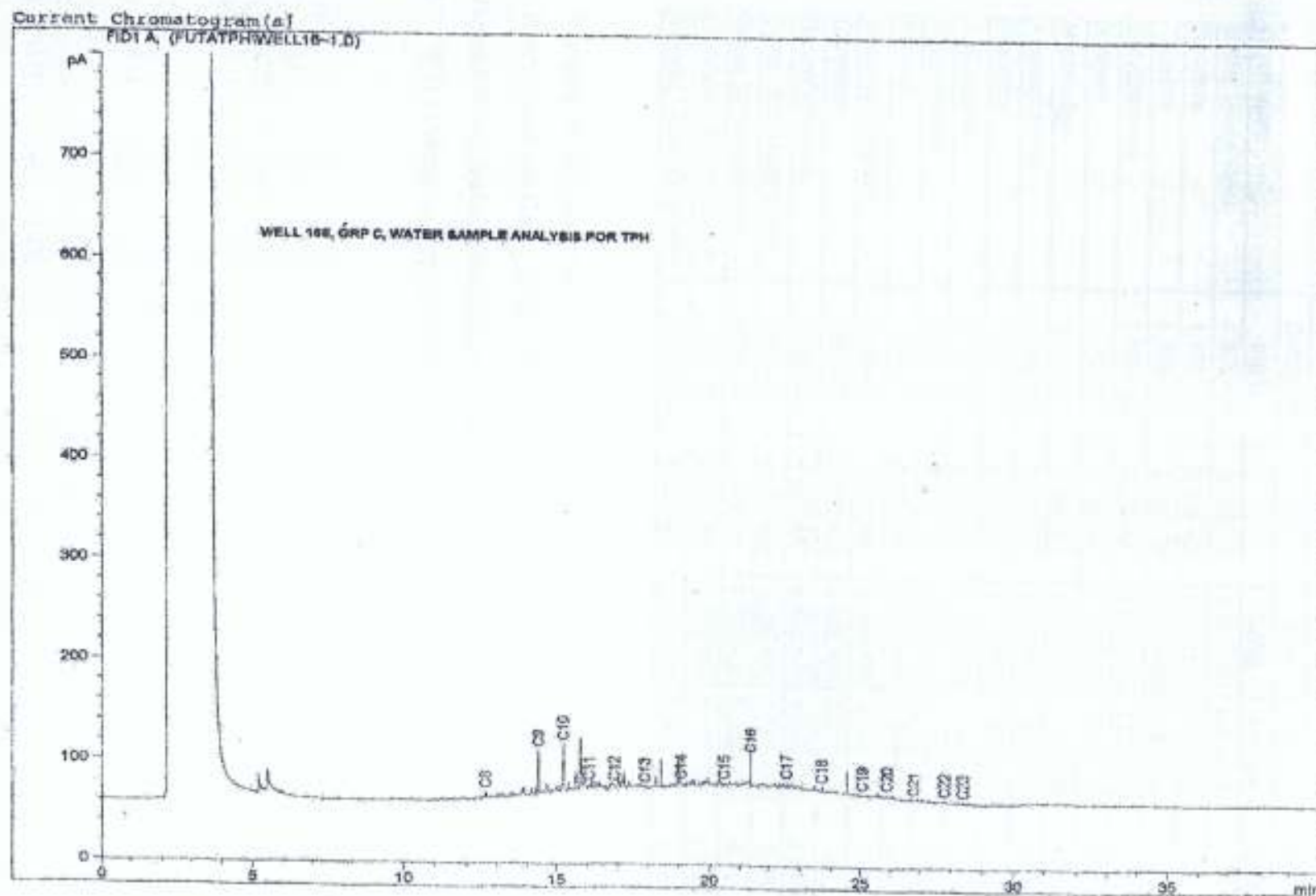


Table 1: Chemical Parameters

Constituent	Solubility mg/L	Hd	Koc L/Kg	D _{i,w} cm ² /s	WQB-7 ug/L
Methyl t-Butyl Ether	4.80E+04	2.40E-02	1.20E+01	9.40E-06	30
Benzene	1.75E+03	2.28E-01	6.17E+01	9.80E-06	5
Toluene	5.26E+02	2.72E-01	1.40E+02	8.60E-06	1,000
Ethylbenzene	1.69E+02	3.23E-01	2.04E+02	7.80E-06	700
Xylenes	1.75E+02	2.76E-01	2.45E+02	8.75E-06	10,000
Naphthalene	3.10E+01	1.98E-02	1.19E+03	7.50E-06	28
Acenaphthene	4.24E+00	6.36E-03	4.90E+03	7.89E-06	420
Flourene	1.98E+00	2.61E-03	7.71E+03	7.88E-06	280
Anthracene	4.34E-02	2.67E-03	2.35E+04	7.74E-06	2100
Flouranthene	2.06E-01	6.60E-04	4.91E+04	6.35E-06	280
Pyrene	1.35E-01	4.51E-04	6.80E+04	7.24E-06	210
Benzo(a)Anthracene	9.40E-03	1.37E-04	3.58E+05	9.00E-06	0.48
Chrysene	1.60E-03	3.88E-03	3.98E+05	6.21E-06	48
Benzo(a)Pyrene	1.62E-03	4.63E-05	9.89E+05	9.00E-06	0.048
Benzo (b)Fluoranthene	1.50E-03	4.55E-03	1.23E+06	5.56E-06	0.48
Benzo (k) Fluoranthene	8.00E-04	3.40E-05	1.23E+06	5.56E-06	4.79
Dibenzo(a,h) Anthracene	2.49E-03	6.03E-07	1.79E+06	5.18E-06	0.048
Indeno(1,2,3,c,d)Pyrene	2.20E-05	6.56E-05	3.47E+06	5.66E-06	0.48

D_{i,w} free-solution diffusion coefficient [L²/T].

H_d Henry's Law constant [atm.L³/mol]

K_{oc} Octanol-Water partition coefficient [L³/M].

WQB-7 W.H.O Water quality standard

Table 2: Derived Chemical Parameters

Conversions	Koc	Koc	foc 0.006	foc 0.001	Di,w	Di,w
Constituent	L/Kg	M ³ /g	Kd-sand	Saturated	cm ² /s	m ² /d
Methyl t-Butyl Ether	1.20E+01	1.20E-05	7.21E-08	1.20E-08	9.40E-08	8.12E-05
Benzene	6.17E+01	6.17E-05	3.70E-07	6.17E-08	9.80E-06	8.47E-05
Toluene	1.40E+02	1.40E-04	8.40E-07	1.40E-07	9.60E-06	7.43E-05
Ethylbenzene	2.04E+02	2.04E-04	1.22E-06	2.04E-07	7.80E-06	6.74E-05
Xylenes	2.45E+02	2.45E-04	1.47E-06	2.45E-07	8.75E-06	7.56E-05
Naphthalene	1.19E+03	1.19E-03	7.15E-06	1.19E-08	7.50E-06	6.48E-05
Acenaphthene	4.90E+03	4.90E-03	2.94E-05	4.90E-08	7.89E-06	6.84E-05
Flourene	7.71E+03	7.71E-03	4.82E-05	7.71E-08	7.88E-06	6.81E-05
Anthracene	2.35E+04	2.35E-02	1.41E-04	2.35E-05	7.74E-06	6.69E-05
Flouranthene	4.91E+04	4.91E-02	2.95E-04	4.91E-05	6.35E-06	5.49E-05
Pyrene	6.80E+04	6.80E-02	4.08E-04	6.80E-05	7.24E-06	6.26E-05
Benzo(s)Anthracene	3.58E+05	3.58E-01	2.15E-03	3.58E-04	9.00E-06	7.78E-05
Chrysene	3.98E+05	3.98E-01	2.39E-03	3.98E-04	8.21E-06	5.37E-05
Benzo(a)Pyrene	9.89E+05	9.89E-01	5.81E-03	9.89E-04	9.00E-06	7.78E-05
Benzo (b) Fluoranthene	1.23E+06	1.23E+00	7.38E-03	1.23E-03	5.58E-06	4.80E-05
Benzo (k) Fluoranthene	1.23E+06	1.23E+00	7.38E-03	1.23E-03	5.56E-06	4.80E-05
Dibenzo(a,h) Anthracene	1.79E+06	1.79E+00	1.07E-02	1.79E-03	5.18E-06	4.48E-05
Indeno(1,2,3,c,d)Pyrene	3.47E+06	3.47E+00	2.08E-02	3.47E-03	5.86E-06	4.89E-05

Paired t test

This function gives a paired Student t test, confidence intervals for the difference between a pair of means and, optionally, limits of agreement for a pair of samples (Armitage and Berry, 1994; Altman, 1991).

The paired t test provides an hypothesis test of the difference between population means for a pair of random samples whose differences are approximately normally distributed. Please note that a pair of samples, each of which are not from normal a distribution, often yields differences that are normally distributed.

The test statistic is calculated as:

$$t = \frac{\bar{d}}{\sqrt{s^2/n}}$$

- where $\bar{d}$ is the mean difference, s^2 is the sample variance, n is the sample size and t is a Student t quantile with $n-1$ degrees of freedom.

Table 3: CRITICAL VALUES of t

df =

1-10, 11-20, 21-30, 31-40, 41-50, 51-60, 61-70, 71-85, >85

	Level of Significance for a Directional Test				
	0.05	0.025	0.01	0.005	0.0005
	Level of Significance for a Non-directional Test				
df	-	0.05	0.02	0.01	0.001
1	6.31	12.71	31.82	63.66	636.58
2	2.92	4.30	6.96	9.92	31.60
3	2.35	3.18	4.54	5.84	12.92
4	2.13	2.78	3.75	4.60	8.61
5	2.02	2.57	3.36	4.03	6.87
6	1.94	2.45	3.14	3.71	5.96
7	1.89	2.36	3.00	3.50	5.41
8	1.86	2.31	2.90	3.36	5.04
9	1.83	2.26	2.82	3.25	4.78
10	1.81	2.23	2.76	3.17	4.59
Top	Level of Significance for a Directional Test				
	0.05	0.025	0.01	0.005	0.0005
	Level of Significance for a Non-directional Test				
df	0.10	0.05	0.02	0.01	0.001
11	1.80	2.20	2.72	3.11	4.44
12	1.78	2.18	2.68	3.05	4.32
13	1.77	2.16	2.65	3.01	4.22
14	1.76	2.14	2.62	2.98	4.14
15	1.75	2.13	2.60	2.95	4.07
16	1.75	2.12	2.58	2.92	4.01
17	1.74	2.11	2.57	2.90	3.97
18	1.73	2.10	2.55	2.88	3.92
19	1.73	2.09	2.54	2.86	3.88
20	1.72	2.09	2.53	2.85	3.85
Top	Level of Significance for a Directional Test				
	0.05	0.025	0.01	0.005	0.0005
	Level of Significance for a Non-directional Test				

df	0.10	0.05	0.02	0.01	0.001
21	1.72	2.08	2.52	2.83	3.82
22	1.72	2.07	2.51	2.82	3.79
23	1.71	2.07	2.50	2.81	3.77
24	1.71	2.06	2.49	2.80	3.75
25	1.71	2.06	2.49	2.79	3.73
26	1.71	2.06	2.48	2.78	3.71
27	1.70	2.05	2.47	2.77	3.69
28	1.70	2.05	2.47	2.76	3.67
29	1.70	2.05	2.46	2.76	3.66
30	1.70	2.04	2.46	2.75	3.65

APPENDIX D: Field-Scale Model Calibration for Hydrocarbon Source Concentration

The injection period was set at 1994 by model calibration. At six months (6 months after injecting BTEX of 872 g/l), the simulated plume attained a steady state configuration with source dissolved concentration of about 550mg/l (Figure 1). The injected total BTEX concentration of 872g/l for the field-scale model was obtained by model calibration/back calculation and fitting the field hydrocarbon concentration observations to the simulated hydrocarbon isoconcentration contours for the period of field sampling and testing (year 2006). To obtain the injected/released hydrocarbon concentration, that fits the site contamination history of twelve years from 1994 to the sampling and field testing period (2006), several total BTEX injected concentrations were tried on the Computer simulation model (Table 1). These tested injection concentration values are multiples of the approximate average density of the hydrocarbon contaminant (BTEX). The injected concentration of 872 g/l was able to simulate in twelve years the maximum observed hydrocarbon concentration (100 mg/l) in well 20 during the year 2006 of field sampling and testing (Figure 4).

Table 1: Injected BTEX concentrations for Field-Scale Model and Simulation Results

Simulation Time (years)						
0	(Injected Concentration)	87.2 g/l	436 g/l	872 g/l	4360 g/l	8720 g/l
0.5	(Max. Observed Concentration)	105 mg/l	200 mg/l	550 mg/l	1020 mg/l	1800 mg/l
12	(Max. Observed Concentration)	18 mg/l	45 mg/l	100 mg/l	430 mg/l	730 mg/l
20	(Max. Observed Concentration)			35 mg/l		
40	(Max. Observed Concentration)			10 mg/l		
60	(Max. Observed Concentration)			0.5 mg/l		

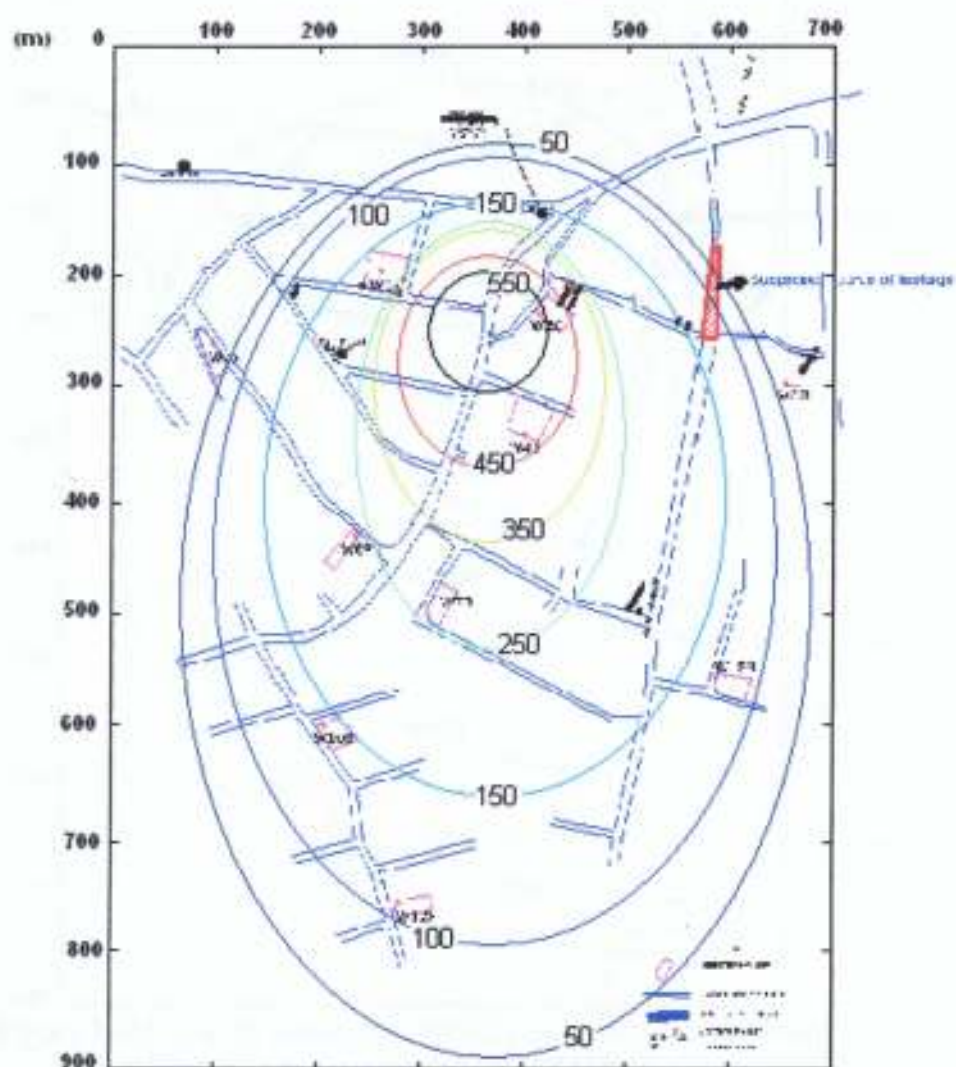


Figure 1: 0.5 year [6 months] of BTEX (mg/l) simulation (1994)

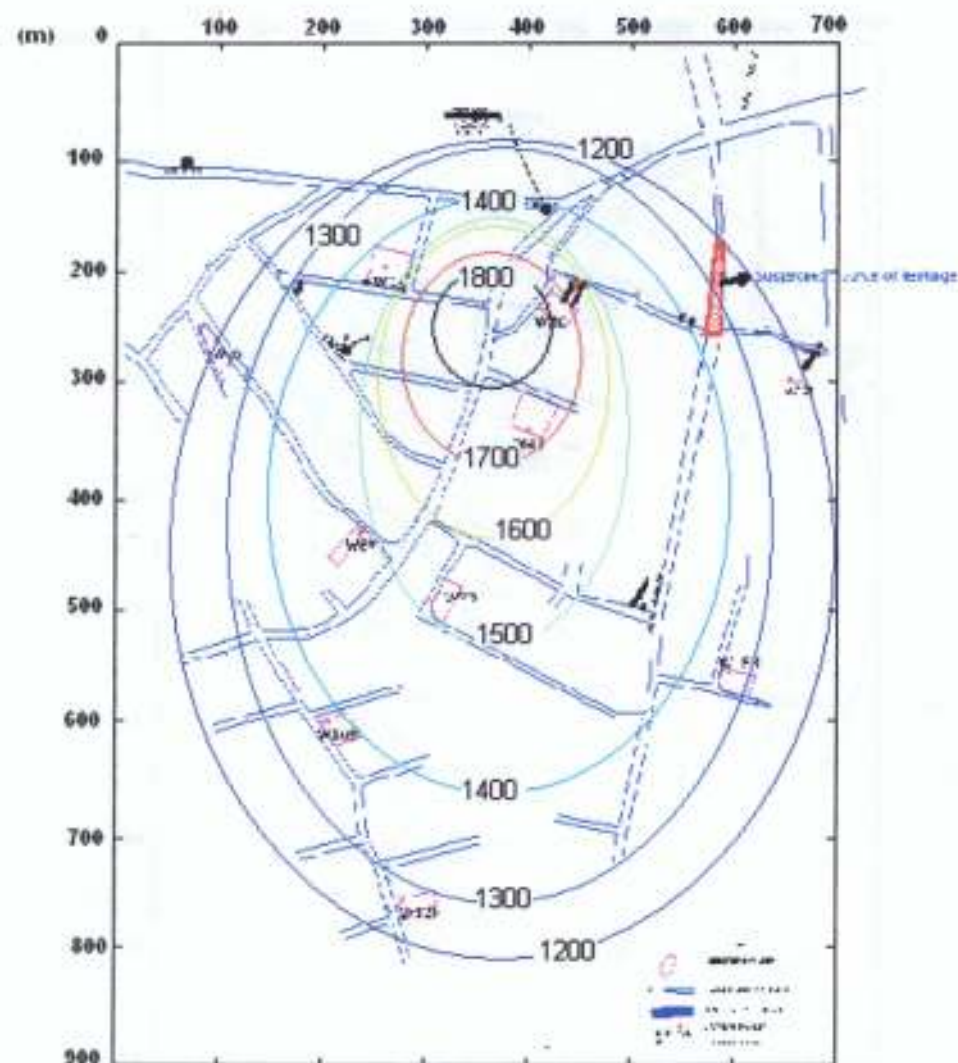


Figure 2: 0.5 year [6 months] of BTEX (mg/l) simulation (1994)
 {Using Injected concentration of 8720 g/l}

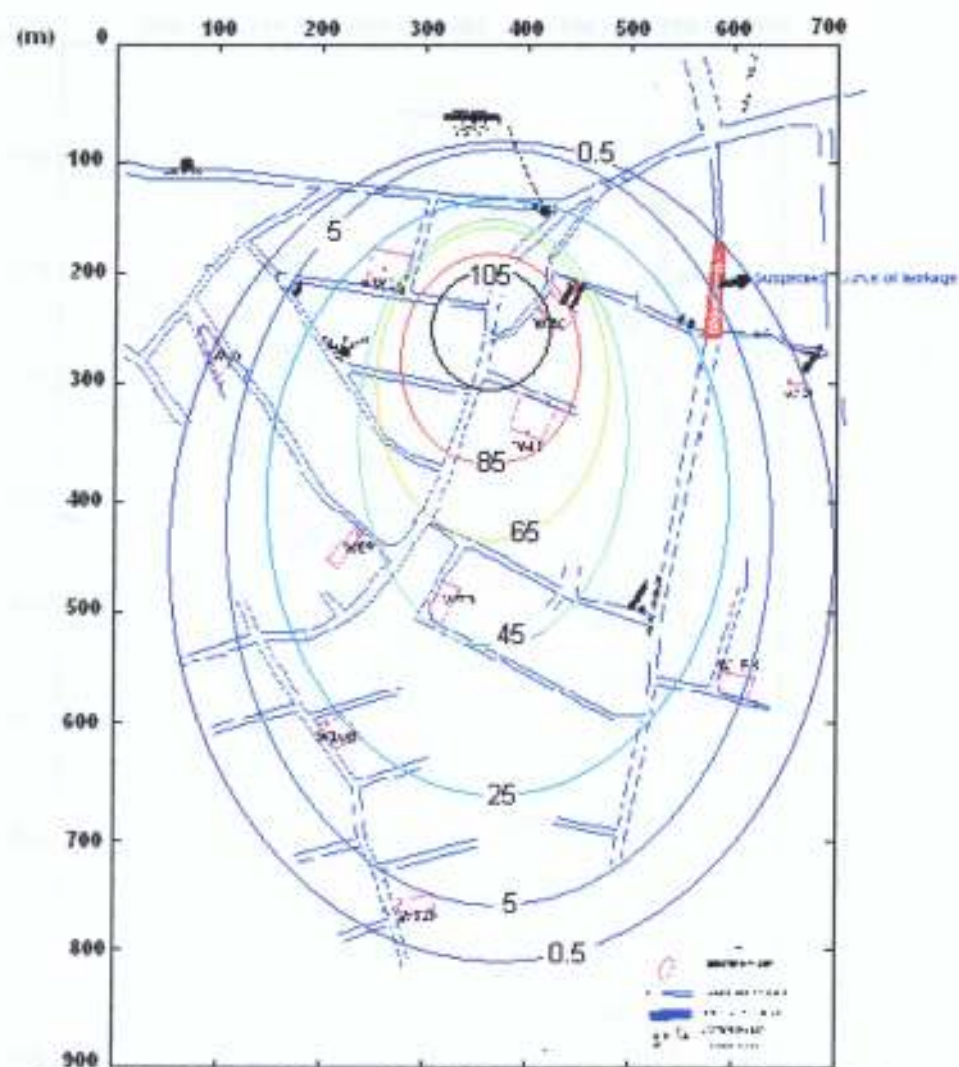


Figure 3: 0.5 year [6 months] of BTEX (mg/l) simulation (1994)
 {Using Injected concentration of 87.2 g/l}

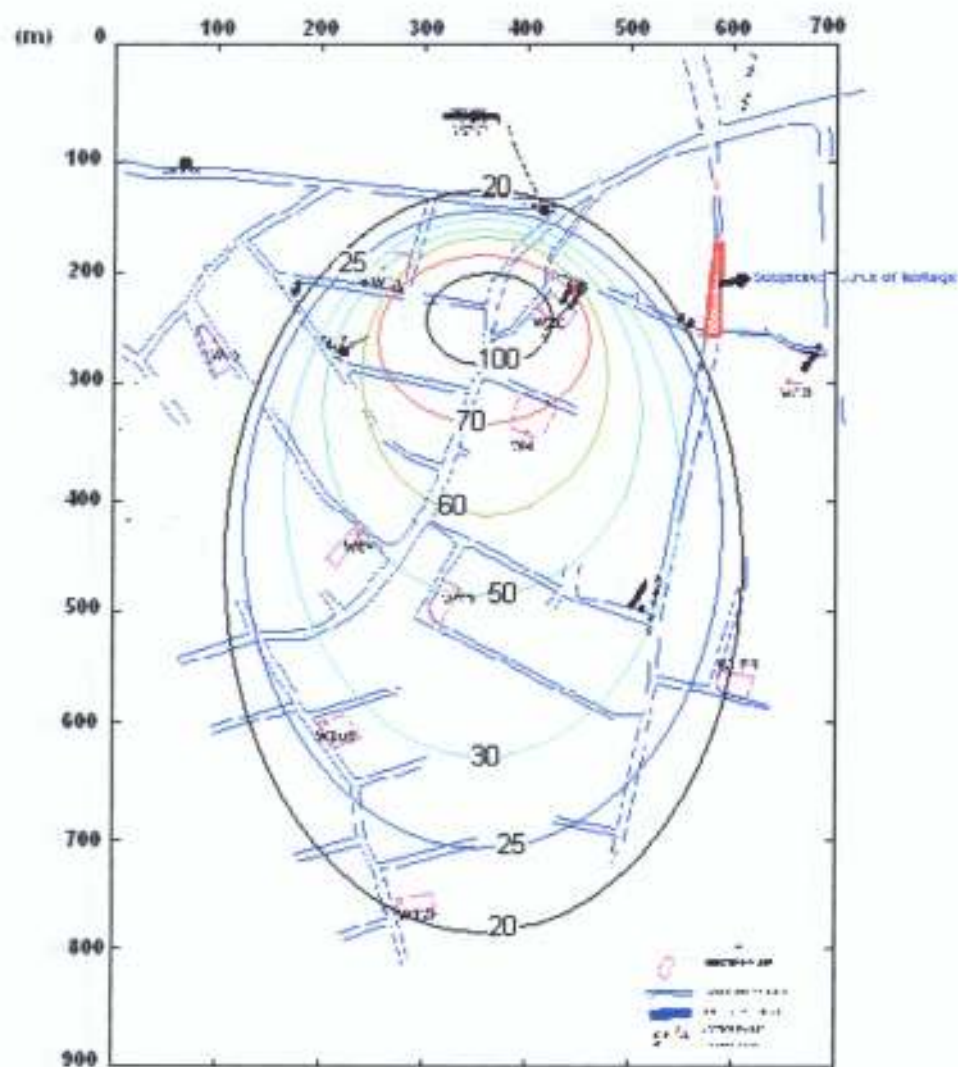


Figure 4: 12 years of BTEX (mg/l) simulation (2006)
 {Using Injected concentration of 872 g/l}

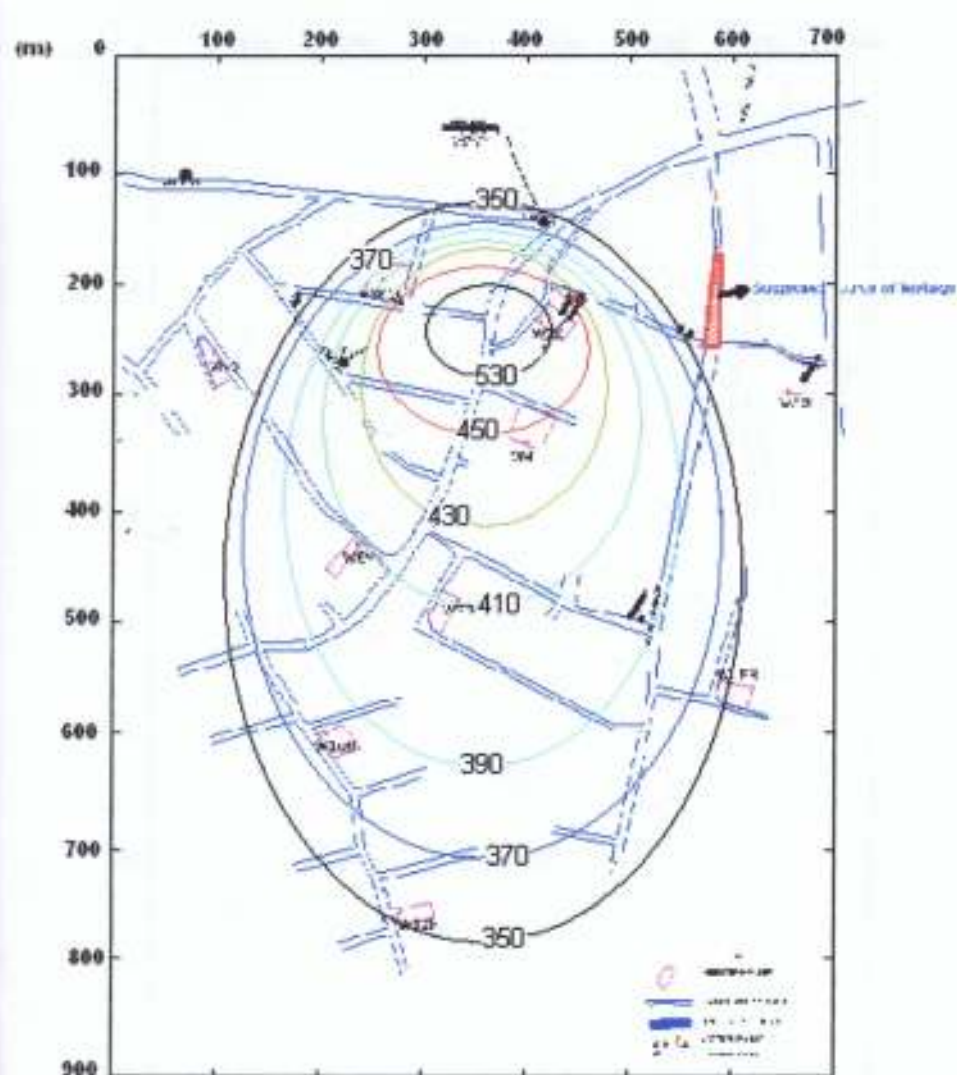


Figure 5: 12 years of BTEX (mg/l) simulation (2006)
 {Using Injected concentration of 8720 g/l}

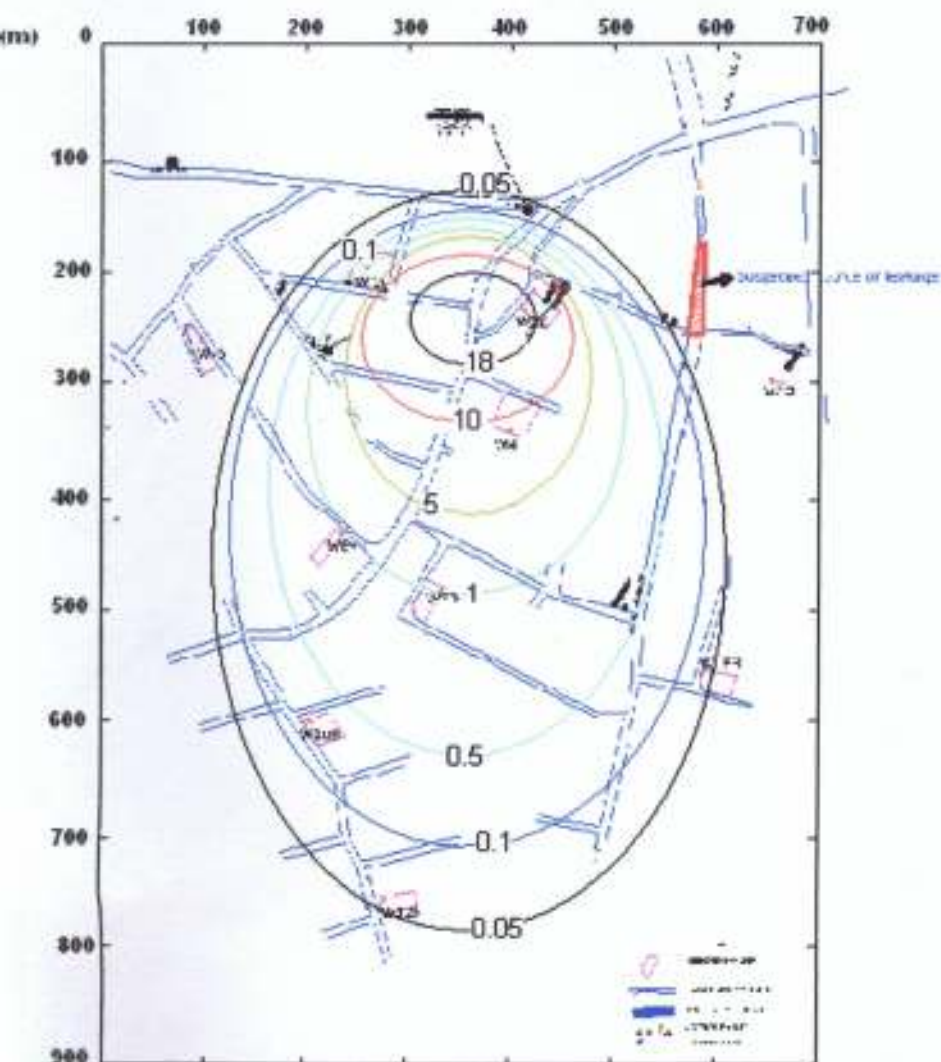


Figure 6: 12 years of BTEX (mg/l) simulation (2006)
 {Using Injected concentration of 87.2 g/l}