

**ENHANCED BIOREMEDIATION OF DISSOLVED AROMATIC HYDROCARBONS
WITHIN A GASOLINE SOURCE AREA USING NITRATE AND
OXYGEN AS ELECTRON ACCEPTORS**

by

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ABSTRACT

Controlled releases of API 91-01 gasoline within 4 m² sheet-piling cells, laboratory studies and numerical simulations were used to investigate the enhanced bioremediation of dissolved aromatic hydrocarbons (BTEXTMB) derived from a gasoline source area under mixed electron-acceptor conditions. The main objective of the research was to evaluate nitrate-based bioremediation as a remedial technology in a gasoline source area under highly-controlled experimental conditions. Gasoline was released into two treatment cells (70 L per cell) in the Borden aquifer to create gasoline-contaminated source areas below the water table, and then water amended with different combinations of electron acceptors was flushed vertically through the cells. One cell received a mixture of NO₃⁻ and microaerophilic O₂ (ca. 2 mg/L dissolved O₂), and the other cell, a control, received microaerophilic O₂ only. Aromatic-hydrocarbon and electron-acceptor utilization as well as other geochemical indicators of biotransformation were then monitored during both flushing and static periods over a 13 month period. Laboratory microcosm experiments and microbial characterization studies were also performed with both pristine and contaminated aquifer material to augment the findings based on *in situ* observations.

Although the consumption of electron acceptors and production of metabolites suggested that microbial activity had been stimulated in the treatment cells, field and laboratory data indicated overall that nitrate-based bioremediation was not an effective source-area remedial technology under the conditions established in this study. Nitrate utilization was slow relative to the residence time in the treatment cell, and preferential utilization of the labile aromatic hydrocarbons was not apparent. Based on laboratory data, the addition of microaerophilic O₂ may have led to the degradation of compounds that otherwise would have been recalcitrant under anaerobic, denitrifying conditions, but the effect *in situ* appeared to be small relative to the mass of gasoline hydrocarbons in the cells. Consequently, mass losses did not appear to be enhanced in the cell treated with microaerophilic O₂ and NO₃⁻ relative to the unremediated control, and effluent breakthrough curves were consistent with concentration trends expected to result from abiotic gasoline dissolution. Despite the negative results obtained in this highly-contaminated system, the data suggested that mixed electron acceptors might be more effective during the latter stages of an enhanced bioremediation project when source-area concentrations were lower, or for downgradient plume control using a reactive wall or other semi-passive remedial technology.

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TABLE OF CONTENTS

<i>ABSTRACT</i>	iv
<i>CHAPTER 1. INTRODUCTION</i>	1
1.1 <i>Objectives</i>	1
1.2 <i>Overview of Experimental Approach</i>	4
1.2.1 <i>Laboratory Experiments</i>	5
1.2.2 <i>Field Experiment</i>	6
1.3 <i>Background Literature</i>	6
1.3.1 <i>Biotransformation Under Single Electron-Acceptor Conditions</i>	6
1.3.2 <i>Biotransformation Under Mixed Electron-Acceptor Conditions</i>	9
<i>CHAPTER 2. STUDY AREA</i>	15
<i>CHAPTER 3. EXPERIMENTAL METHODS</i>	19
3.1 <i>Aquifer Core Collection</i>	19
3.2 <i>Laboratory Microcosm Experiments</i>	19
3.2.1 <i>General Set Up Procedures</i>	19
3.2.2 <i>Acetylene Block</i>	22
3.3 <i>Microbial Characterization</i>	23
3.3.1 <i>Enumerations</i>	23
3.3.2 <i>Microbial Dehydrogenase Activity</i>	24
3.4 <i>Borden Field Experiment</i>	25
3.4.1 <i>Instrumentation</i>	25
3.4.2 <i>Gasoline Injection</i>	28
3.4.3 <i>Experimental Design</i>	34
3.4.4 <i>Field Sample Collection</i>	39
<i>CHAPTER 4. LABORATORY EXPERIMENTS</i>	46
4.1 <i>Microcosm Experiments: Pristine Borden Sand</i>	46
4.1.1 <i>Microcosm Experiment 1</i>	49

4.1.2	<i>Microcosm Experiment 2</i>	54
4.2	<i>Microcosm Experiments: Gasoline-Contaminated Borden Sand</i>	60
4.2.1	<i>Microcosm Experiment 3</i>	60
4.3	<i>Microbial Characterization Results</i>	78
4.3.1	<i>Pristine Aquifer Material</i>	78
4.3.2	<i>Gasoline-Contaminated Aquifer Material</i>	80
4.4	<i>Discussion and Conclusions</i>	83
CHAPTER 5.	<i>FIELD EXPERIMENT</i>	89
5.1	<i>Overview of Results</i>	89
5.1.1	<i>Flow Characteristics</i>	89
5.1.2	<i>Dissolved Oxygen and Nitrate</i>	90
5.1.3	<i>Organics</i>	98
5.1.4	<i>Nitrite Production</i>	110
5.1.5	<i>Metabolite Production</i>	112
5.2	<i>Mass Balance Results</i>	117
5.3	<i>Simulation of Aromatic Hydrocarbon Breakthrough Curves</i>	121
5.4	<i>Discussion and Conclusions</i>	145
6.0	<i>CONCLUSIONS AND IMPLICATIONS</i>	152
REFERENCES		155
APPENDIX A.	<i>GASOLINE CHARACTERISTICS</i>	167
APPENDIX B.	<i>TRACER TEST</i>	175
APPENDIX C.	<i>ANALYTICAL METHODS</i>	188
APPENDIX D:	<i>AQUIFER MONITORING RESULTS</i>	193
APPENDIX E:	<i>MASS BALANCE CALCULATIONS</i>	196

LIST OF TABLES

	page
2-1 Chemistry of unamended groundwater at the experimental site	18
3-1 Summary of microcosm designs used in the study	20
3-2 Summary of API 91-10 gasoline spike test	45
4-1 Summary of major conclusions from laboratory experiments	47
4-2 Design summary, Experiment 1	50
4-3 Percent of individual aromatic hydrocarbons remaining in active, low-BTEXTMB concentration microcosms relative to sterile controls	52
4-4 Design summary, Experiment 2	55
4-5 Microbial enumerations and hydrocarbon degrading activity after reamendment on day 163, Experiment 2	59
4-6 Design summary, Experiment 3	62
4-7 Percent of individual aromatic hydrocarbons remaining in active, low- and high-BTEXTMB concentration microcosms relative to sterile controls	73
4-8 Dissolved nitrous oxide concentrations in selected microcosms containing contaminated aquifer material from the Nitrate Cell	75
4-9 Microbial enumerations of Borden cores	79
4-10 Experimental design: ETS activity in pristine and contaminated aquifer material	82
5-1 Hydrocarbon component classes in API 91-01 gasoline and gasoline-contaminated core extract samples	111
5-2 Detected organic acids and phenols in API 91-01 gasoline and groundwater	113
5-3 Concentrations in mg/L of selected redox-sensitive constituents in the experimental cells and injection water	115
5-4 Nitrate mass balance results for 174-day flushing experiment	118
5-5 Aromatic hydrocarbon mass balance	119

	page
5-6 UNIFAC activity coefficients for selected API 91-01 gasoline constituents	127
5-7 Gasoline mass estimates from RME analysis.	136
A-1 Mole fractions of identified compounds in API 91-01 gasoline	169
A-2 Characteristics of API 91-01 gasoline	172
A-3 Comparison of measured concentrations of aromatic hydrocarbons in API 91-01 gasoline.	173
A-4 Measured and calculated concentrations of aromatic hydrocarbons in water equilibrated with API 91-01 gasoline at 10°C	174
B-1 Comparison of bromide concentrations determined from a bromide electrode and ion chromatography (IC)	178
B-2 Bromide tracer test results	179
D-1 Environmental monitoring downgradient of wastewater treatment mound and treatment cells	194

LIST OF ILLUSTRATIONS

	page
2-1 Location map of the study area at CFB Borden (from Oliveira (1997))	16
3-1 Plan view of treatment cells with surveyed locations of instrumentation	26
3-2 Plan view of study area	29
3-3 Vertical profiles of water saturation prior to the gasoline injections	30
3-4 Vertical profiles of total dissolved BTEXTMB in the Nitrate Cell on November 22-26, 1995, approximately one month after gasoline injection	32
3-5 Vertical profiles of total dissolved BTEXTMB in the Control Cell on November 22-26, 1995, approximately one month after gasoline injection	33
3-6 Injection system schematic for the Nitrate Cell	35
3-7 Record of injection rates over the 174-day flushing experiment	37
3-8 Schematic of groundwater sample collection apparatus	40
4-1 Nitrate, NO ₂ ⁻ , D.O., and normalized total BTEXTMB concentrations in Experiment 1 microcosms	51

	page
4-2 Nitrate, NO ₂ ⁻ , D.O., and total BTEXTMB concentrations in Experiment 2 microcosms	56
4-3 BTEXTMB concentrations in individual replicates for each of the treatment groups in Experiment 2	57
4-4 Normalized D.O. and total BTEXTMB concentrations in sterile microcosms with and without gasoline-contaminated aquifer material from the Nitrate Cell (Experiment 3)	64
4-5 Nitrate, NO ₂ ⁻ , D.O., and total BTEXTMB concentrations in active and sterile control microcosms with gasoline-contaminated aquifer material from the Nitrate Cell (Experiment 3)	65
(a) Aerobic (high O ₂) treatment	66
(b) Microaerophilic (low-O ₂) treatment	67
(c) Microaerophilic, 10x BTEXTMB dilution treatment	68
4-6 Normalized concentrations of selected aromatic hydrocarbons in gasoline-contaminated microaerophilic microcosms amended with gasoline-saturated water	69
4-7 Normalized concentrations of selected aromatic hydrocarbons in gasoline-contaminated microaerophilic microcosms amended with 10x dilution of gasoline-saturated water	70
4-8 Normalized concentrations of selected aromatic hydrocarbons in sterile, gasoline-contaminated microaerophilic microcosms	71
4-9 Normalized toluene concentrations in gasoline-contaminated aquifer material	76
4-10 Numbers of denitrifiers, aerobic heterotrophs, and benzene-toluene degraders in pristine and contaminated aquifer material	81
4-11 Accumulation of INT formazan as a measure of ETS activity in pristine and contaminated aquifer material	84
5-1 Injection and extraction D.O. concentrations	91
5-2 D.O. concentrations at 60- and 180-cm bgs ports during the 174-day flushing experiment	92
5-3 D.O. concentrations collected from the extraction well and adjacent multilevel piezometer in the Nitrate Cell	94

	page	
5-4	Vertical profiles of D.O. during and after the 174-day flushing experiment	95
5-5	Injection NO ₃ ⁻ concentrations	96
5-6	Nitrate concentrations in injection water and 60- and 180-cm bgs ports during the 174-day flushing experiment	97
5-7	Nitrate concentrations during the static period between flushing experiments	99
5-8	Concentrations of dissolved aromatic hydrocarbons in samples collected from extraction-well ports	100
5-9	Concentrations of aromatic hydrocarbons in samples collected from the extraction-well expressed as percentages of concentrations in water equilibrated with fresh API 90-01 gasoline	102
5-10	Vertical profiles of benzene and total BTEXTMB before, during, and after the flushing experiments	103
5-11	Concentrations of dissolved aromatic hydrocarbons at individual 180-cm bgs ports in the Nitrate Cell during the 174-day flushing experiment	104
5-12	Concentrations of dissolved aromatic hydrocarbons at individual 180-cm bgs ports in the Control Cell during the 174-day flushing experiment	105
5-13	Corrected toluene, ethylbenzene, and NO ₃ ⁻ concentrations from a selected piezometer in the Nitrate Cell that was sampled during the static period	107
5-14	Vertical profiles of residual BTEXTMB in the Nitrate Cell	108
5-15	Vertical profiles of residual BTEXTMB in the Control Cell	109
5-16	Model domain for coupled dissolution / solute-transport model	122
5-17	Representation of API 91-01 composition used in dissolution model	125
5-18	Calculated vs. measured BTEXTMB concentrations in gasoline-saturated water	129
5-19	Example of dissolution model output for 70 L API 91-01	131
5-20	Concentration ratios in effluent of Nitrate Cell	134
5-21	Concentration ratios in effluent of Control Cell	135
5-22	Retardation factor sensitivity analysis	141
5-23	Simulated and measured effluent breakthrough curves in the Nitrate Cell	143
5-24	Simulated and measured effluent breakthrough curves in the Control Cell	144

	page
B-1 Normalized bromide concentrations in samples of injection and extraction water during bromide tracer test (Nitrate Cell)	180
B-2 Normalized bromide concentrations in samples of injection and extraction water during bromide tracer test (Control Cell)	181
B-3 Measured bromide breakthrough curves at 60-cm bgs ports in the Nitrate Cell	182
B-4 Measured and calculated bromide breakthrough curves at 120-cm bgs ports in the Nitrate Cell	183
B-5 Measured and calculated bromide breakthrough curves at 180-cm bgs ports in the Nitrate Cell	184
B-6 Measured bromide breakthrough curves at 60-cm bgs ports in the Control Cell	185
B-7 Measured and calculated bromide breakthrough curves at 120-cm bgs ports in the Control Cell	186
B-8 Measured and calculated bromide breakthrough curves at 180-cm bgs ports in the Control Cell	187
E-1 Concentration contour plot of total BTEXTMB in Nitrate Cell	202

CHAPTER 1. INTRODUCTION

1.1 Objectives

In North America leaking gasoline storage tanks are a major source of groundwater contamination. Gasoline and other fuels contain several regulated compounds, most notably benzene, a suspected human carcinogen. Spilled gasoline is typically trapped in the vicinity of the water table as immobile, non-aqueous phase liquid (NAPL). Because soluble gasoline constituents partition to groundwater, the NAPL is a long-term source of groundwater contamination. Since the early 1970s, when the inefficiencies of physical-removal methods were becoming widely recognized, there has been intense interest in using indigenous microorganisms to remediate gasoline spills. Although gasoline is a complex mixture of hundreds of compounds of varying toxicity, most remediation activities in the groundwater industry have focused on the soluble hydrocarbon constituents (Chapelle, 1999). The aromatic hydrocarbons benzene, toluene, ethylbenzene, xylene isomers, trimethylbenzene isomers, and naphthalene (referred to as BTEXTMB in this thesis) are relatively soluble, and therefore constitute the majority of the mass that partitions to groundwater to form contaminant plumes. These constituents are also more toxic and mobile in groundwater than other fuel constituents.

Historically engineered approaches such as enhanced *in situ* bioremediation have been used to remediate hydrocarbon-contaminated aquifers (Chapelle, 1999). These approaches have typically involved injecting electron acceptors such as dissolved O₂ and nutrients into contaminated regions of an aquifer to stimulate indigenous microorganisms. Given its low solubility and high reactivity in groundwater, delivering a sufficient quantity of O₂ to the contaminated region has been a major limitation of enhanced bioremediation. Another significant limitation is an inability to achieve adequate mixing between the injected fluid and the contaminated groundwater in the subsurface (Chapelle, 1999). More recently there has been increasing reliance on intrinsic biological and physical-mixing processes for plume remediation (i.e., natural attenuation). However, when intrinsic biological processes are relied upon for site restoration, anaerobic plumes may persist for long periods of time. This is because O₂ is replenished only by weak dispersive mixing along the plume boundaries (MacQuarrie et al. 1989). If continued site monitoring is required for regulatory compliance, natural attenuation can be an expensive option (Lovely, 1997),

particularly if the source area has been left intact. For both enhanced and intrinsic bioremediation approaches, anaerobic biotransformation processes can therefore play an important role in limiting contaminant migration and expediting aquifer restoration. In this study nitrate (NO_3^-) was investigated as an alternate electron acceptor for enhanced bioremediation. Nitrate salts are very soluble and less reactive in anaerobic environments, and NO_3^- provides a high energy yield to denitrifying bacteria; as such it may be useful as a replacement or supplement to O_2 in oxygen-limited aquifers. As the sole electron acceptor, NO_3^- also has limitations, the most significant being the recalcitrance of benzene (Chapelle, 1999). In addition, because NO_3^- is a regulated compound its fate must also be considered.

The longevity of a groundwater plume is controlled in part by the amount of hydrocarbon mass in the source area. A reduction of both the source mass and the mass flux into the aquifer, and an acceleration of the rate of depletion of soluble constituents from the NAPL are some of the potential benefits of stimulating microbial activity in a source area. Relatively little source-area bioremediation research has been reported in the peer-reviewed literature, however, and the effectiveness of electron-acceptor addition, particularly for alternate electron acceptors such as NO_3^- , remains unclear. Chapelle (1999) attributes this to difficulties in separating hydrodynamic effects, such as dilution, from biotransformation processes. The main objective of this study was to evaluate, under controlled, experimental conditions, nitrate-based bioremediation as a remedial technology for dissolved aromatic hydrocarbons within a gasoline source area. It was hypothesized that a denitrifying population capable of rapid aromatic-hydrocarbon biotransformation would develop in response to extended NO_3^- exposure, and therefore that NO_3^- could be used to stimulate mass loss.

A second objective was to determine whether aromatic-hydrocarbon mass losses would be more extensive in the presence of mixed electron acceptors. Accordingly, in most of the experimental treatments low levels of dissolved O_2 were present with NO_3^- to potentially stimulate the oxidation of compounds such as benzene that are recalcitrant under denitrifying conditions. It has been hypothesized by some researchers that so-called microaerophilic dissolved O_2 concentrations (defined here as concentrations below 2 mg/L) could be utilized for the initial oxidation of the aromatic ring (e.g., Wilson and Bouwer, 1997). This would yield partially-oxidized intermediates susceptible to oxidation under anaerobic, denitrifying conditions further

downgradient, and result overall in enhanced mass removal. To date, however, relatively little research has been performed under mixed electron-acceptor conditions, and the field-scale controls are poorly understood. It seems likely that there are significant limitations under field conditions, such as O₂ utilization by microorganisms growing on non-target organic compounds in the presence of multiple substrates, and abiotic O₂ demand from reduced metal species. Nonetheless, the effects of microaerophilic O₂ warranted further consideration because even a small enhancement could be beneficial to a nitrate-based bioremediation project. These hypotheses cannot be addressed adequately under the relatively-uncontrolled conditions that typically prevail at real fuel spill sites.

Although both laboratory and field experiments were undertaken, the main focus of this thesis was a field-scale demonstration of enhanced source-area bioremediation. As a well-controlled, dynamic system, the field demonstration was expected to provide the most realistic assessment of this remediation technology. The experiment was conducted in the Borden aquifer located at Canadian Forces Base Borden, Ontario. Two controlled gasoline spills were used to generate source areas, and then water amended with different combinations of NO₃⁻ and O₂ was flushed through the gasoline-contaminated regions to evaluate the extent of mass loss of the soluble, plume-forming aromatic hydrocarbons. One treatment cell received microaerophilic O₂ and NO₃⁻, and the other, a control, received microaerophilic O₂ only. It was hypothesized that the number of aromatic hydrocarbons undergoing transformation and the overall amount of the mass loss would be greater in the cell treated with mixed electron acceptors. Because the treatment cells were unreplicated and subject to considerable experimental uncertainty, multiple lines of evidence were used in an attempt to identify the key processes within each treatment cell, and demonstrate the effects of the experimental variables.

These lines of evidence included *in situ* observations (concentrations of organic substrates, amended electron-acceptors, other geochemical indicators of biotransformation, and metabolites) as the field experiment progressed, coring at the completion of the experiment to estimate the amount of aromatic-hydrocarbon mass remaining in the cells, laboratory studies, and numerical simulations of the field data. Laboratory microcosm experiments provided useful data that could not be obtained readily at the field scale; in these experiments the extent of biotransformation was investigated under a relatively wide range of experimental conditions. After the field experiment

was completed, a microcosm experiment with core material from the cell amended with NO_3^- was also performed to verify field observations. Additional laboratory work was done during various stages of the project to enumerate key fractions of the microbial population in the aquifer material, and investigate changes in biomass and dehydrogenase activity in response to gasoline exposure. Following the experimental work, a simple one-dimensional dissolution/solute-transport model was used to simulate the breakthrough curves obtained in the field. These different lines of evidence were then used to evaluate the effectiveness of this remedial approach in the Borden aquifer.

This thesis is organized as follows: The Borden field site is described in Chapter 2. Descriptions of the field and laboratory methods used in the study are included in Chapter 3. Results and discussion of laboratory experiments, including both microcosm studies and microbial characterization work, are provided in Chapter 4. Results and discussion of the field experiment and one-dimensional dissolution/flow model are provided in Chapter 5. The overall conclusions and implications of the research are discussed in Chapter 6. A description of the physical and chemical characteristics of the API 91-01 gasoline is included in Appendix A. A description of procedures and results of the field tracer test designed to evaluate the flow of injected water in the treatment cells is provided in Appendix B. Appendix C includes descriptions of laboratory sampling and analytical procedures, as well as analytical procedures used for samples collected in the field. Appendix D includes results of the groundwater sampling performed downgradient of the wastewater treatment mound and treatment cells to monitor potential releases to the aquifer. Mass balance calculations are provided in Appendix E. The laboratory and field data presented graphically in this thesis are tabulated in Appendix F.

1.2 Overview of Experimental Approach

An overview of the experimental activities, including the chronology, rationale, and objectives of the individual experiments is provided in the following two subsections.

1.2.1 Laboratory Experiments

Prior to the initiation of this thesis, a series of preliminary laboratory experiments were performed by other University of Waterloo researchers using pristine Borden aquifer material. This work was done to obtain baseline data on the effects of dissolved O₂, inorganic nutrients, NO₃⁻ concentration, and electron-acceptor mixtures in microcosms with low concentrations (10x dilution of gasoline-saturated water) of aromatic hydrocarbons. Results and interpretation of these preliminary microcosm experiments are presented, along with other project results, in the Final Report prepared for the U.S. EPA (Barbaro et al., 1998). Enumerations of denitrifiers and aerobic heterotrophs were also performed on numerous Borden cores in support of these experiments; in contrast to other preliminary data these results have been included in this thesis (Table 4-9) because they provide a good indication of the distribution of these microbial populations in pristine aquifer material.

After the gasoline was spilled in the field, it became apparent that aromatic-hydrocarbon concentrations would be higher than a tenfold dilution of gasoline-saturated water throughout the treatment cells, and so an additional series of microcosm experiments was performed using gasoline-saturated groundwater (about 100 mg/L total aromatics) and pristine aquifer material. The first such experiment (Experiment 1) was performed to compare the response of the aquifer material to high (gasoline-saturated water) and low (10x dilution of gasoline-saturated water) concentrations under the mixed electron-acceptor conditions in the field (microaerophilic O₂ plus NO₃⁻). Because the added O₂ was rapidly consumed in Experiment 1, a second experiment (Experiment 2) was performed with pristine aquifer material to determine whether high concentrations of aromatics would degrade under fully-aerobic conditions.

After the flushing experiments were completed, cores were collected from the treatment cells for additional laboratory work. A follow-up microcosm experiment (Experiment 3) was performed using material from the Nitrate Cell to further investigate the extent of biotransformation in aquifer material that had been exposed to gasoline for nearly two years, and potentially verify field observations. Additional microbial enumerations and a dehydrogenase activity assay were also performed to determine whether there were detectable changes in the microbial community in response to gasoline exposure.

1.2.2 Field Experiment

The flushing experiment began in May, 1996, approximately six months after the gasoline-contaminated zones were created, and continued for 174 days. During this period groundwater amended with electron acceptors was injected continuously into the two treatment cells. Target vertical groundwater velocities and cell residence times were about 25 cm/day and 10 days, respectively. The "Nitrate Cell" received mixed electron acceptors (NO_3^- and dissolved O_2), and the "Control Cell" dissolved O_2 only to investigate the effect of NO_3^- addition in a low O_2 environment. During operation, flow rates and dissolved solute concentrations (electron-acceptors, aqueous aromatic hydrocarbons, and other redox-sensitive species) were measured periodically. In November, 1996, pumps were shut off and the cells were sampled periodically under static conditions for organics and electron acceptors.

In May, 1997, the treatment cells were flushed again for 24 days. Although previous studies have indicated that denitrifying activity is not nutrient limited in the Borden aquifer (Barbaro et al., 1998), a nutrient solution was pumped into both cells during this period to determine whether NO_3^- and aromatic-hydrocarbon utilization could be enhanced. The concentration of dissolved O_2 injected into the cells was also increased. For clarity, these phases are referred to in this thesis as "the 174-day flushing experiment", "the static period", and "the 24-day flushing experiment". Groundwater samples were also collected near the end of the experiment for analysis of partially-oxidized intermediates (metabolites). In July and August, 1997, additional aquifer cores were collected to complete a mass balance on the aromatic compounds and assess the extent of biotransformation mass loss.

1.3 Background Literature

1.3.1 Biotransformation Under Single Electron-Acceptor Conditions

Aerobic Conditions. Under aerobic conditions, petroleum hydrocarbons, including aromatic hydrocarbons, are readily degraded by indigenous groundwater microorganisms (e.g., Barker et al., 1987). Aerobic degradation rates are controlled at the plume scale by the aquifer properties that control O_2 transport to the contaminated area (MacQuarrie et al., 1989), rather than by

limitations of microbial metabolism. As a remediation technology, the major limitation of aerobic biotransformation is the inability to deliver sufficient O₂ to the contaminated area. Oxygen replenishment is limited by its low solubility (ca. 11 mg/L D.O. in equilibrium with air at 10°C) and high reactivity with reduced species such as iron (Fe) (Morgan and Watkinson, 1992).

At low concentrations, the kinetics of dissolved O₂ utilization may dramatically limit the rate of oxygen uptake and aromatic-hydrocarbon degradation. It has been commonly observed that the rate of O₂ uptake is independent of concentration at high O₂ concentrations, but below some critical value, uptake rates become dependent on concentration (e.g., Johnson, 1967). The concentration of dissolved O₂ has also been observed to limit substrate degradation rates (Larson et al., 1981; Shaler and Klecka, 1986; Chiang et al., 1987; Leahy and Olsen 1997). The threshold or critical O₂ concentration is often characterized by the half-saturation constant (K_{d_0}), which is defined as the concentration at which the respiration rate is one half the maximum rate. Shaler and Klecka (1986) compiled K_{d_0} values for various oxygenases responsible for either ring fission or initial hydroxylation of the aromatic ring. They found that these values were high (up to 2.2 mg/L) relative to those for metabolism of small, easily-degraded compounds such as glucose or acetate, for which O₂ is required mainly as the terminal electron acceptor for the cytochrome oxidase. They postulated that high concentrations were consistent with the dual role of O₂ as both cosubstrate (i.e., addition of oxygen atoms to the aromatic ring during initial oxidation steps) and electron acceptor in this type of transformation reaction. On the other hand, microorganisms adapted to a low O₂ environment may synthesize enzyme systems designed to more efficiently utilize O₂ (e.g., a monooxygenase system with lower half-saturation constants) (Leahy and Olsen, 1997). Wilson and Bouwer (1997) found that critical O₂ concentrations, compiled from sixteen studies, ranged from 0.013 to 1.5 mg/L, with the lower values generally corresponding to utilization of simple substrates such as glucose.

If broadly applicable, these findings have important implications for a remedial approach that relies upon low levels of dissolved O₂ to initiate oxidation of recalcitrant organics. If the half-saturation concentrations for O₂ utilization are high, rates of substrate utilization will begin dropping at relatively high O₂ concentrations, and substantial threshold O₂ concentrations may persist, or the remaining O₂ may be utilized by other strains growing on simpler non-target

substrates. More work is needed to clarify this issue, however, because even a small mass-loss enhancement may contribute significantly to the overall success of a remediation program.

Denitrifying Conditions. Studies performed over the past 10 years have suggested that NO_3^- addition is a potentially viable bioremediation technology (e.g., Kuhn et al., 1988; Hutchins et al., 1991a; Hutchins et al., 1991b; Barbaro et al., 1992; Reinhard et al., 1997). With NO_3^- as sole electron acceptor, however, results among various studies have not been consistent, and several potential limitations have been identified.

Perhaps the major limitation associated with NO_3^- addition is the frequent persistence of benzene under anaerobic, denitrifying conditions (Berry-Spark et al., 1986; Hutchins, 1991a; Hutchins, 1991b, Barbaro et al., 1992; Reinhard et al., 1997). On the other hand, benzene has been shown to biodegrade under denitrifying conditions in the Major et al. (1988) study which utilized Borden aquifer sediment. While the possibility of experimental artifact (e.g., microcosm leakage) cannot be ruled out, benzene loss was not observed in active, anaerobic controls incubated under identical conditions. In other studies with Borden aquifer material (Berry-Spark et al. 1986; Barbaro et al., 1992), as well as at other sites (Hutchins, 1992a), it was noted that the addition of acetylene gas substantially inhibited aromatic hydrocarbon biotransformation. In the Major et al. (1988) study, however, BTX-degrading activity was less affected by the addition of acetylene. Their data showed that the accumulation of nitrous oxide corresponded to the period when BTX was declining, and that NO_3^- was required for BTX disappearance. These results raise the possibility that the experimental design of Major et al. (1988) selected for a distinct denitrifying population with the metabolic capability to biodegrade benzene.

Previous studies have also shown varying levels of removal of the toluene, ethylbenzene, and the xylene isomers. For instance, using aquifer sediment from Park City, Kansas, Hutchins (1991a) found that toluene, ethylbenzene, *m*-xylene, and *p*-xylene were biodegraded under denitrifying conditions to below 5 $\mu\text{g/L}$ in batch microcosms. In contrast, in the field experiment performed by Barbaro et al. (1992), a toluene threshold concentration of 50 to 100 $\mu\text{g/L}$ persisted throughout the experiment, and ethylbenzene and xylenes removal was on the order of only 50% of injection concentrations, despite the continued presence of NO_3^- . Because the aromatic hydrocarbons are regulated compounds, threshold concentrations are potentially problematic.

A second limitation involves the incomplete mineralization of monoaromatic hydrocarbons under limited O₂ or anaerobic conditions. Partially-oxidized compounds may form under both aerobic (Barker et al., 1987) and anaerobic conditions (Cozzarelli et al., 1995; Barbaro et al., 1992; Cozzarelli et al., 1990), but they appear to be most persistent, and therefore accumulate, in O₂-depleted environments. Metabolite production under denitrifying conditions has been demonstrated in laboratory studies with pure cultures (Evans et al., 1992; Kuhn et al., 1988). These compounds are mobile and geochemically reactive. If persistent, their presence may adversely affect bioremediation systems based on anaerobic, NO₃⁻ utilization.

Another potential problem is the degradation of non-target organic compounds in preference to aromatic hydrocarbons. Hutchins (1991a) noted that the extent of BTEX mass loss was lower in aquifer material contaminated with JP-4 jet fuel relative to uncontaminated material spiked with BTEX. The NO₃⁻ demand was much larger in the JP-4 contaminated material, suggesting that non-target organics were being utilized in preference to BTEX. Similar observations were made by Reinhard et al. (1995) in the hydrocarbon-contaminated Seal Beach aquifer. Barbaro et al. (1992) arrived at similar conclusions, although in that study it appeared that NO₃⁻ was being used either as an assimilatory source of N and/or as an electron acceptor to oxidize naturally-occurring organic matter in preference to low concentrations of BTEX. Although the biotransformation of other fuel constituents can be considered a positive result, insufficient microbial utilization of the mobile, regulated compounds may limit this technology.

1.3.2 Biotransformation Under Mixed Electron-Acceptor Conditions

Background. The major anticipated advantage of biotransformation under mixed electron-acceptor conditions is enhanced mass loss, particularly of compounds such as benzene that are recalcitrant under denitrifying conditions. Because much less work has been done under these conditions, the advantages and limitations discussed in this section are still quite speculative, particularly for *in situ* applications where an indigenous microbial population mediates reactions.

From research on their population ecology and growth strategies, most denitrifiers are facultatively-anaerobic, heterotrophic bacteria that grow readily under aerobic conditions and prefer to utilize O₂ as electron acceptor. Historically there has been considerable debate regarding

the effect of O_2 on denitrifying activity. The conventional view was that denitrifying activity did not begin until O_2 was nearly depleted (Tiedje, 1982; Tiedje, 1988), and many researchers considered denitrification a strictly anaerobic process. There is also considerable recent evidence that denitrification proceeds in the presence of substantial amounts of O_2 (Krul, 1976; Robertson and Kuenen, 1984; Lloyd et al., 1987; Bonin and Gilewicz, 1991; Lloyd, 1993; Patureau et al., 1994; Carter et al., 1995). Although aerobic denitrification is now a well-established phenomenon, the regulating mechanisms and physiological significance of the process are still not well understood, and the biochemical diversity of denitrifiers makes generalization difficult. Wilson and Bouwer (1997) provide a comprehensive review of the aerobic denitrification literature.

Under mixed O_2/NO_3^- conditions, O_2 appears to be the most important variable. If the dissolved O_2 concentration is initially high, then there will be considerable aerobic biotransformation, but denitrifying activity will be reduced or completely inhibited. Current research indicates that the critical dissolved O_2 concentration above which denitrification is completely inhibited varies over a broad range (0.02 to 7.7 mg/L) (Wilson and Bouwer, 1997). The critical concentration is thought to be species, enzyme, and substrate specific, and probably dependent on growth conditions. Alternatively, if the dissolved O_2 concentration is low, rates of aerobic respiration will be low or negligible, and denitrifying activity will probably dominate. As discussed in Section 1.1.2, the critical O_2 concentration for supporting aerobic degradation of aromatic substrates appears to be in the range of 1-2 mg/L, with considerable variation among species and substrates. It should be noted that additional complexity may be present *in situ*; dissolved O_2 concentrations measured in bulk pore water may not be indicative of the O_2 levels in microsites or biofilms.

If the O_2 concentration is initially high (e.g., 10 mg/L), NO_3^- could be used to enhance aerobic microbial activity and growth by serving as an assimilatory source of nitrogen (Van 'T Riet, et al., 1968), but, as discussed above, dissimilatory NO_3^- reduction would probably be inhibited. Once dissolved O_2 concentrations fell below the critical value for inhibiting denitrifying activity, NO_3^- could then be utilized as the electron acceptor. The major advantage of high initial O_2 concentrations would appear to be relatively extensive aerobic biotransformation. A second possible advantage would be a larger population of denitrifiers resulting from aerobic growth of

facultative anaerobes (Su and Kafkewitz, 1994). It should be noted, however, that the regions of aerobic and denitrifying activity would probably be separated spatially at the plume scale, diminishing the benefit of this effect, with most O₂ depletion occurring near the point of injection, and NO₃⁻ depletion over a longer downgradient flowpath.

Of greater interest for nitrate-based bioremediation is the behavior of a mixture consisting of NO₃⁻ and microaerophilic dissolved O₂ concentrations. Under microaerophilic conditions, it is less likely that the concentration of dissolved O₂ would be inhibitory to denitrifiers. As a consequence, denitrifying activity could occur in the presence of low levels of O₂; the denitrification rate, however, may be significantly reduced. There are two potential advantages to a mixture consisting of NO₃⁻ and microaerophilic O₂. If the target compound is degradable under denitrifying conditions, NO₃⁻ can be used by facultative anaerobes to relieve the electron-acceptor deficit imposed by O₂ consumption (Mikesell et al., 1993; Leahy and Olsen, 1997); this circumvents the problem of re-oxygenating the subsurface. More importantly for bioremediation of aromatic hydrocarbons, it has been hypothesized that the O₂ could participate in reactions and contribute to the complete oxidation of otherwise recalcitrant compounds such as benzene (Britton, 1989; Wilson and Bouwer, 1997).

Based on the current literature, the benefits associated with microaerophilic O₂ are unclear. If the concentration of dissolved O₂ is below the critical value to support O₂-linked respiration, then there would be negligible aerobic degradation of recalcitrant compounds like benzene (Section 1.3.1). Even if all of the O₂ was consumed (i.e., the K_{d0} was low), the stoichiometry of the reaction would appear to constrain the extent of aerobic oxidation. For example, if the aerobic reaction proceeds to CO₂, complete utilization of 2 mg/L O₂ mineralizes only 0.65 mg/L benzene to CO₂. Benzene mass loss would be reduced further if the O₂ consumption was spread among other aqueous substrates (i.e., aromatic hydrocarbons). In fact, in laboratory experiments with Borden sand, *m*-xylene is commonly biodegraded first under aerobic conditions (Barbaro et al., 1998). Alternatively, some researchers have hypothesized that, rather than supporting aerobic respiration, low levels of dissolved O₂ could be utilized only as a substrate for oxygenase enzymes (Britton, 1989). This mechanism has been proposed as a means of initiating aromatic ring oxidation, yielding partially-oxidized intermediates susceptible to further oxidation by a

denitrifying pathway. There is currently no evidence that the so-called "sparing effect" has enhanced the biotransformation of aromatic compounds *in situ*.

From an engineering perspective, a mixture of microaerophilic O_2 / NO_3^- is the optimal combination. This circumvents the problems associated with adding high O_2 concentrations and relies mostly on soluble NO_3^- as the oxidant. At the field scale, however, there are potential limitations to adding microaerophilic O_2 concentrations. First, in most contaminated aquifers multiple substrates are present, including aromatics, other hydrocarbons, and natural organic material. It is conceivable, therefore, that the O_2 added to an aquifer will be utilized completely by microorganisms growing on non-target compounds. Second, the abiotic O_2 demand must be considered. As noted by Kennedy and Hutchins (1992), if the aquifer is initially anaerobic, reduced metal species may exert a large O_2 demand, leading to scavenging of O_2 intended for bioremediation, and metal precipitation on injection equipment. Finally, some strains of denitrifiers have been shown to be very sensitive to dissolved O_2 (Hernandez and Rowe, 1987), so it is possible that even a low concentration of O_2 *in situ* may inhibit denitrifying activity.

Application to Fuel-Contaminated Sites. The published laboratory studies on biotransformation of aromatic hydrocarbons under mixed electron acceptor conditions have yielded ambiguous results. Major et al. (1988) found that BTX mass loss in microcosms with Borden aquifer sediment was slightly enhanced in the presence of both NO_3^- and O_2 relative to losses in aerobic microcosms. They speculated that the NO_3^- alleviated a nitrogen limitation during aerobic metabolism, or that denitrification was occurring within anaerobic microsites. In a pure culture study, Su and Kafkewitz (1994) found that *Pseudomonas maltophilia* was capable of degrading toluene and xylene isomers in the presence of NO_3^- and a 98:2 / $N_2:O_2$ atmosphere. Miller and Hutchins (1995) used laboratory columns to study BTEX removal from three different aquifer sands under NO_3^- only and then NO_3^- / O_2 conditions. In two of the columns, adding low levels of O_2 did not enhance BTEX removal, and in the third, O_2 had an inhibitory effect. Under all conditions, benzene was completely recalcitrant. Hutchins et al. (1992b) also used laboratory columns to study the effects of various combinations of NO_3^- / O_2 on the removal of BTEX from aquifer material. They found that adding NO_3^- to the column with low O_2 decreased TEX breakthrough by an order of magnitude, demonstrating that NO_3^- was needed to increase substrate utilization. There were no adverse effects associated with low levels of O_2 . Benzene removal was

low and independent of electron-acceptor conditions. In contrast, Wilson et al. (1995) observed benzene degradation in the presence of 2 mg/L dissolved O_2 and NO_3^- , but only toluene degradation under anaerobic, denitrifying conditions.

Anid et al. (1993) investigated BTEX removal in aerobic columns amended with either hydrogen peroxide or NO_3^- . In columns amended with NO_3^- , effluent dissolved O_2 concentrations dropped from 9 mg/L to 2 mg/L and 164 mg/L NO_3^- was consumed. Benzene was recalcitrant in these columns, but in additional experiments with NO_3^- and <1 mg/L O_2 , approximately 25 percent of added benzene appeared to biodegrade. In this aquifer material, strict anaerobic conditions did not appear to be required for NO_3^- reduction, although the formation of anaerobic microsites cannot be ruled out. In addition, benzene removal was enhanced under anaerobic rather than aerobic conditions. Leahy and Olsen (1997) showed that NO_3^- enhanced the rate of toluene utilization by denitrifying strains after the dissolved O_2 fell below a critical concentration. Denitrifying strains were able to maintain a higher rate of toluene utilization by switching to denitrifying activity when the availability of dissolved O_2 was low. Similarly, Mikesell et al. (1993) and Hutchins (1991c) both demonstrated in the laboratory that, under limited O_2 conditions, biotransformation of certain aromatics could be enhanced by the presence of NO_3^- . In the Hutchins (1991c) study, benzene losses were observed in microcosms amended with both O_2 / NO_3^- after the apparent removal of O_2 .

Since the late 1980s, only a handful of nitrate-based bioremediation field studies have been completed (Sheehan et al., 1988; Hutchins et al., 1991b; Battermann and Meier-Lohr, 1995; Hutchins et al., 1995; Reinhard et al., 1995; Reinhard et al., 1997; Vroblesky et al., 1997). Hutchins et al. (1991b) added NO_3^- and O_2 via an infiltration gallery to an aquifer in Traverse City, MI contaminated with JP-4 jet fuel. Both electron acceptors were consumed, and more NO_3^- was consumed than required for BTX degradation, indicating that other compounds were also being utilized under denitrifying conditions. Toluene and xylenes degradation appeared to be stimulated in the aquifer, but benzene removal was apparently due only to flushing. Hutchins et al. (1995) describe the performance of a nitrate-based bioremediation system applied to a petroleum spill in Park City, Kansas. In that study, NO_3^- utilization was confirmed but site heterogeneities obscured the performance evaluation. Although laboratory data indicated that the aromatic hydrocarbons would biodegrade under denitrifying conditions, this could not be confirmed in the field. This

study showed the problems that can arise in evaluating the extent of bioremediation in heterogeneous aquifers.

Battermann and Meier-Lohr (1995) describe the performance of a large-scale NO_3^- plus O_2 bioremediation system at an abandoned refinery site contaminated with residual hydrocarbons (aqueous BTEX concentrations 10 to 100 mg/L). After three years of operation, about 300 metric tons of hydrocarbons were removed, of which 80 percent were attributed to biotransformation and 20 percent to flushing. During pilot-scale tests at the same site, Battermann et al. (1994) found that hydrogen peroxide was attenuated near the infiltration point. Nitrate, on the other hand, was distributed over much larger contaminated areas; in the first year of operation, approximately 100 mg/L NO_3^- was consumed over a 50-day residence time.

These field studies suggested that ambient dissolved O_2 in the injected water does not inhibit denitrifying activity, but there were no observable benefits associated with O_2 either. The extent of aerobic biotransformation near source areas or the effects of lower concentrations of O_2 further downgradient are not easily assessed in uncontrolled field situations. Moreover, it is difficult to determine the contribution of flushing as a mass-removal mechanism. The highly-controlled field experiment used in this study provided additional information on the *in situ* utilization of O_2 following injection to a hydrocarbon source area.

CHAPTER 2. STUDY AREA

The field research was conducted at CFB Borden, Ontario (Figure 2-1). The research area is located in an abandoned sand pit. The depth to groundwater varies from ground surface to about 1.5 meters below ground surface depending on the location within the pit and the season. The site has been studied extensively over the past 17 years. The geology and local hydrogeology were investigated by MacFarlane et al. (1983). The hydrogeology and groundwater chemistry of the sand pit were discussed in detail by Mackay et al. (1986).

The sand pit is underlain by a relatively homogeneous, unconfined sand aquifer composed of interbedded fine- to medium-grained glaciolacustrine sand. Analysis of a bulk sample indicates that the aquifer material is composed of 58% quartz, 19% feldspars, 14% carbonates, 7% amphiboles, and 2% chlorite (Mackay et al., 1986). The aquifer is about nine meters thick, extending from ground surface to a clay layer. Detailed coring and hydraulic-conductivity testing have shown that the deposit consists of near-horizontal beds of contrasting hydraulic conductivity that range in thickness from a few centimeters to tens of centimeters, and in length from one to a few meters (Sudicky, 1986). The mean hydraulic conductivity is 7×10^{-3} cm/sec, with variations between layers occasionally exceeding two orders of magnitude (Sudicky, 1986). The mean weight-fraction of organic carbon (f_{oc}) was estimated at 0.00018, and the porosity at 0.33 (Mackay et al. 1986). The spatial variability of porosity based on 36 samples was found to be small (coefficient of variation = 0.05).

A dense, woody peat layer was encountered at the experimental site at a depth of about 2.7 m below ground surface. Based on cores and other drilling information, this layer was about 10 cm thick, fairly continuous, and overlain by about 25 cm of dark gray, dense silty sand. Elevated dissolved methane (CH_4) and sulfide (HS^-) were frequently detected in groundwater samples collected near the peat layer, and cores of the peat sequence had a sulfide odor and were dark gray with orange oxidation zones on the upper and lower boundaries. To avoid pumping water across this sequence, all experiments were conducted within the top 2.5 m of the aquifer. As a low-hydraulic-conductivity layer, this sequence may have limited the flux of water from the underlying aquifer when the flushing experiments were in progress.

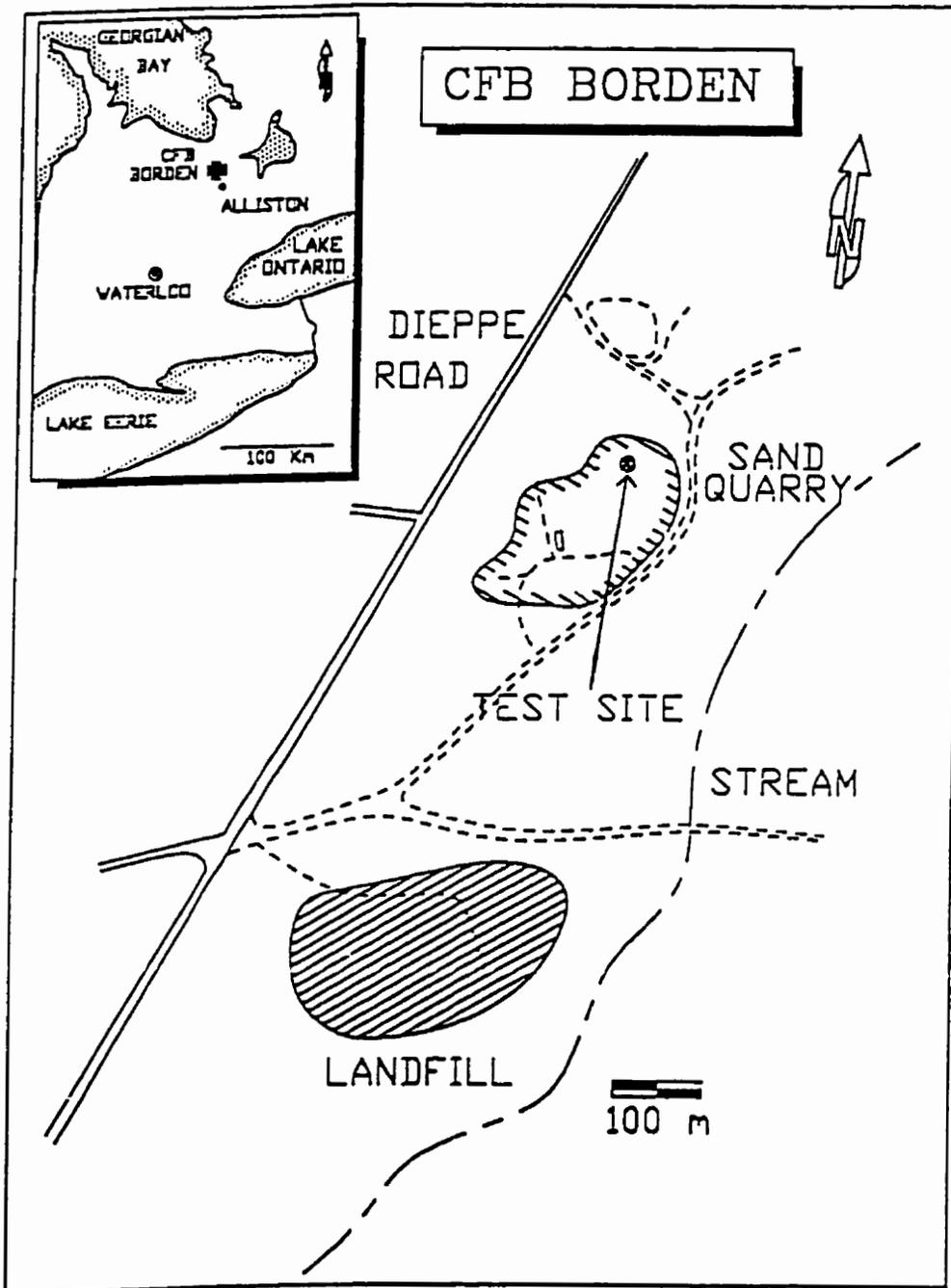


Figure 2-1. Location map of the study area at CFB Borden (from Oliveira (1997)).

Groundwater flows in a northeasterly direction at about 9 cm/day, and remains near 10°C throughout the year. A leachate plume originating from an abandoned municipal landfill is present at the base of the unconfined aquifer, at depths ranging from five to seven meters below ground surface. Groundwater above the leachate plume is unaffected by the landfill.

Based on locations of previous experimental activities, the site has never been exposed to aromatic hydrocarbons. Although the presence and depth of the landfill leachate plume beneath the site was not determined, groundwater chemistry data collected from a shallow well (2.49 m depth) indicated that the landfill leachate, if present, was below the experimental zone. Dissolved O₂ levels in shallow groundwater were unexpectedly low at about 0.2 mg/L; in other regions of the sand pit, shallow groundwater has substantially higher concentrations of dissolved O₂ (e.g., Barbaro et al., 1994). There was no detectable Fe or NO₃⁻ in background groundwater, and dissolved organic carbon was low (<2 mg/L). Dissolved Mn was detected in this water, however, and may have exerted an abiotic O₂ demand. The chemistry of the groundwater is summarized in Table 2-1.

Table 2-1. Chemistry of unamended groundwater at the experimental site. Samples collected May, 1996 from shallow, upgradient supply well. Concentrations in mg/L.

Parameter	Concentration
Si	2.88
Cl	3.58
SO ₄	6.31
NO ₃	<0.1
PO ₄	<0.2
Br	<0.1
HCO ₃	258
Ca	80
Mg	3.55
Na	4.21
K	1.16
NH ₄	0.82
Fe	<0.1
Mn	1.24
pH	7.48
DO	0.2
DOC	<2
BTEXTMB	n.d.
Temp (°C)	12.5

n.d. - not detected at individual compound method detection limit (Appendix C).

CHAPTER 3. EXPERIMENTAL METHODS

The experimental procedures used in the laboratory and field are described in this chapter. Descriptions of the procedures used for laboratory microcosm experiments, microbial characterization of the aquifer material, the controlled gasoline spills in the field, and the design and operation of the field experiment are included here.

3.1 Aquifer Core Collection

Aquifer sediment was collected at various times during the study for different purposes. Core material was used for logging the stratigraphy, microcosm and microbial characterization studies, and mass balances on the gasoline injected into the field treatment cells. Cores were obtained in 5.08 cm (2 in) diameter aluminum tubes using either a piston or core catcher. The coring system is described in detail in Zapico et al. (1987).

Aluminum core tubes designated for microbiology experiments were rinsed with methanol and flamed in the field prior to use. After the cores were collected they were sealed tightly, transported within 4 hr to the University of Waterloo, and stored at 4°C. In preparation for laboratory experiments, aquifer material was removed from core tubes either in an anaerobic chamber (gasoline-contaminated core material - Experiment 3) (Lab-Line Instruments, Inc., Model 6550), or a sterile, laminar flow cabinet (pristine core material - Experiments 1 and 2) (Nuair, Inc., Model NU-408FM-300), depending on *in situ* O₂ concentrations, and refrigerated in sterile mason jars. Material adjacent to core-tube walls was discarded or used in sterile control microcosms.

3.2 Laboratory Microcosm Experiments

3.2.1 General Set Up Procedures

All microcosm experiments in this study were performed with crimp-sealed 60-ml glass hypovials. For each sampling event, a set of microcosms was sacrificed for analysis. A set contained replicate microcosms for each treatment group in the experiment. Generally there were

three to five different treatment groups, including a sterile control, per experiment. Each microcosm received 20 g of homogenized aquifer material, groundwater spiked with organic compounds, nutrients, and electron acceptors, if required, and was sealed with a Teflon™-lined septum and an aluminum crimp seal. Depending on the intended O₂ status of the microcosms, a 2-4 ml headspace was present. Preliminary work with this type of set-up indicated that a pure O₂ or air filled headspace was the most reliable means of supplying dissolved O₂ (see below). If O₂ was not required, microcosms were prepared with no headspace. Sterile equipment and aseptic technique were used in all aspects of microcosm preparation and sampling. A summary of the design is provided in Table 3-1. Sampling and analysis procedures are given in Appendix C.

Table 3-1. Summary of microcosm design used in the study.

Type	Description
Sacrificial	60-ml glass hypovials; crimp-sealed; 20 g aquifer material; 2-4 ml pure oxygen or air headspace present in some microcosms; analytes measured in fluid phase (organics, e ⁻ acceptors); set of replicates sacrificed for each sampling event

The source of the organic substrates was API 91-01 gasoline (Appendix A). To prepare gasoline-saturated water, an appropriate volume of uncontaminated Borden groundwater was first sparged for at least 3 hr with either sterile nitrogen gas or sterile air, depending on the treatment. An aliquot of this water was transferred to a sterile separatory funnel. Gasoline was added to yield a 10:1 water to gasoline volume ratio. The separatory funnel was then shaken manually three times (5 min each). After 24 hr, gasoline-saturated water was removed from the funnel to glass bottles for dispensing to microcosms. If lower substrate concentrations were required for an experiment, a 10x dilution of the gasoline-saturated water was performed using an aliquot of the gassed, hydrocarbon-free groundwater. The dissolved O₂ concentration of the prepared water was determined prior to dispensing to microcosms. Measured total BTEXTMB concentrations in gasoline-saturated water ranged from 70-110 mg/L, depending on the experiment. Concentrations differed because for some experiments (i.e., Experiments 1 and 2), gasoline was taken from a storage container where the gasoline volume was small relative to the size of the container.

Consequently, the gasoline phase appeared to be depleted in volatile constituents. In all cases the initial composition of the gasoline-saturated water was determined from samples collected immediately prior to microcosm preparation.

Microcosms were prepared either in the anaerobic chamber or in the sterile flow cabinet. For anaerobic or microaerophilic conditions, aquifer material was dispensed within the anaerobic chamber to avoid any contact with air. For aerobic conditions, aquifer material was dispensed into microcosms in the flow cabinet. Aquifer material was dispensed into sterile control microcosms several days in advance to allow for sterilization (1/2 or 1 hr autoclave run on three consecutive days). After all the aquifer material was dispensed, contaminated groundwater and amendments were added. Microcosms were then filled completely with appropriate solutions and crimp sealed. All microcosms received inorganic nutrients (NH_4Cl and KH_2PO_4) from concentrated, sterile, anaerobic stock solutions to yield 5 mg/L as N, and 2 mg/L as P. Nitrate, where required, was added as a concentrated stock solution of KNO_3 to yield concentrations of 25 mg/L as N. Sterile controls received an additional 0.5 ml of 10% (w/v) sodium azide solution to inhibit microbial activity. In some cases, the nutrients and NO_3^- were spiked into the groundwater before dispensing to microcosms.

Microcosms requiring dissolved O_2 were moved to the sterile flow cabinet after construction, decrimped, and the appropriate volume of water removed with a sterile syringe. "Low" dissolved O_2 microcosms, also referred to as microaerophilic microcosms, received a 2 ml ambient air headspace (Hutchins, 1991a), and "high" dissolved oxygen microcosms, also referred to as aerobic microcosms, contained a 4-ml pure O_2 headspace. Pure O_2 was added by purging the headspace at a rate of approximately 300 ml/min for 30 seconds and quickly replacing the crimp seal. It should be noted that partitioning of the aromatic hydrocarbons to a headspace of this size is minimal. For example, partitioning calculations based on Henry's Law indicate that only 2% of the total mass of benzene would partition to a 4-ml headspace.

The headspace method for establishing "microaerophilic" conditions provided a total mass of about 0.6 mg O_2 (assuming 20% by volume in air) in a microcosm. Measured initial aqueous concentrations in sterile controls were ca. 5 mg/L (Section 4.2.1). It is acknowledged that the initial D.O. concentration in microcosms prepared in this manner exceeded microaerophilic levels

as defined previously in this study (2 mg/L or less). However, to obtain observable results it was necessary to provide a mass of O₂ sufficient to drive aerobic reactions in this static system. A strict adherence to the operational definition of microaerophilic conditions (2 mg/L initial D.O. concentration with no headspace), while ideal, was not tractable with the experimental methods used here. Considering the limitations associated with establishing microaerophilic conditions in a static microcosm, it was concluded that an air headspace provided a reasonable analogue to the dynamic system in the field, where a continuous injection concentration of 2 mg/L O₂ could be maintained.

Sterile aqueous controls (no aquifer material) were also prepared (Experiment 3) to investigate the rate of diffusive loss of dissolved O₂ and BTEXTMB. Microcosms were prepared aseptically with sterile groundwater and amended with 90 mg/L neat BTEXTMB, 0.6 ml sodium azide solution, and dissolved O₂. Two sets of microcosms were prepared: microaerophilic and aerobic. Microaerophilic microcosms contained a 2-ml air headspace, and were incubated in the anaerobic chamber. Aerobic microcosms contained a 4-ml pure-O₂ headspace and were incubated in the laboratory cupboard. These microcosms were stored with other microcosms prepared for Experiment 3 and periodically sampled over a 159-day period to document abiotic losses of dissolved O₂ and organic compounds from sterile microcosms.

After set-up microcosms were stored in the dark at room temperature (23±2°C) either in the anaerobic chamber supplied with a 1% CO₂, 2.5% H₂O, 96.5% N₂ mixed gas, or a laboratory cupboard (aerobic microcosms). Room temperature incubation was unavoidable because the temperature within the anaerobic chamber could not be controlled. Experimental temperatures were therefore roughly twice *in situ* temperatures. Previous experience with Borden aquifer material suggests that temperature does not affect experimental results with respect to compound degradability; compounds that degrade at room temperatures also degrade at groundwater temperatures. Reaction rates are, however, faster at room temperature.

3.2.2 Acetylene Block

The cause of the rapid NO₃⁻ utilization observed in the follow-up microcosm experiment (Experiment 3; Section 4.2) was investigated by assaying for denitrifying activity. Because

acetylene inhibits the reduction of N_2O to N_2 , the accumulation of nitrous oxide in the presence of acetylene is considered strong evidence of denitrification (Tiedje, 1982). Acetylene gas was added to duplicate microcosms from each treatment group that contained NO_3^- by injecting 1% (v/v) through the septum, shaking the vial for 1 min, storing inverted for 1/2 hr to equilibrate the aqueous phase with the headspace, and then quickly replacing the pierced septum. Prior to injection, the acetylene was passed through a series of flasks containing distilled water to remove any acetone that may have been present. These microcosms were incubated in the anaerobic chamber for 15 days and then analyzed for N_2O and acetylene, as well as dissolved O_2 , NO_3^- , nitrite (NO_2^-), and BTEXTMB.

3.3 Microbial Characterization

3.3.1 Enumerations

Aerobic Heterotrophs. Enumerations of viable, aerobic heterotrophic and denitrifying microorganisms were conducted by the standard spread plate and most-probable-number (MPN) methods, respectively, using 0.1% Na-pyrophosphate (pH=7.0) to suspend the aquifer material, and phosphate-buffered saline (1.18 g Na_2HPO_4 , 0.22 g $NaH_2PO_4 \cdot H_2O$, 8.5 g/L NaCl, pH 7) to dilute the suspension as required. R2A medium was used for the aerobic heterotrophic plate counts (HPCs) (Reasoner and Geldreich, 1985). R2A medium is a relatively low-nutrient medium that was developed for the enumeration of microorganisms in potable water. All plates were prepared in triplicate for each dilution, and incubated at room temperature for up to 30 days.

Denitrifiers. For the denitrifier MPN procedure, 18-ml vials were filled with 12 ml 1/10-strength nutrient broth (Difco Laboratories, Detroit, MI), and amended with 2 mM KNO_3 and 0.17% Noble agar (Difco). Immediately prior to inoculation, the medium was deaerated by placing the vials in flowing steam for 5-10 min, then quickly cooled to room temperature and inoculated. Inoculated vials were sealed with sterile, slotted butyl rubber stoppers (Wheaton), and the headspace of each vial was flushed with sterile nitrogen for 30 sec by loosening the stopper slightly and inserting a sterile syringe needle into the stopper slot. Vials were then sealed permanently with an aluminum crimp lid. Finally, 0.6 ml acetylene gas was injected into the headspace using a sterile 1-ml syringe fitted with a membrane filter (0.2 μm pore size). All vials were prepared in

triplicate and incubated at room temperature for up to 61 days. After incubation, 0.1-0.2 ml of culture fluid was removed from each vial and tested with diphenylamine reagent for NO_3^- and/or NO_2^- (Tiedje, 1982). Denitrification was confirmed in approximately 10% of vials with depleted NO_3^- by analyzing for the presence of accumulated N_2O . A 2-ml sample of microcosm headspace gas was analyzed for N_2O as described in Appendix C.

Aerobic Benzene-Toluene Degraders. A suspension of aquifer material was prepared by aseptically adding 10 g (wet wt) of aquifer material to 90 ml 0.1% Na pyrophosphate solution (pH 7). The suspension was shaken for 10 min at 400 rpm on a rotary shaker, then diluted further in phosphate-buffered saline. One ml aliquots of selected dilutions were added to triplicate tubes of a mineral medium (Furukawa et al., 1983) in screw-capped test tubes (10 ml medium/tube). Each tube was then amended with 1 μL of a neat, filter-sterilized benzene/toluene mixture (1:1 concentration ratio) using a micropipettor. The tube was closed and shaken to dissolve the hydrocarbons. Tube caps were covered with a layer of Parafilm and plastic wrap to minimize losses of volatiles during incubation. Resulting maximum aqueous concentrations were about 50 mg/L for both benzene and toluene, although actual concentrations were probably lower due to partitioning into the tube headspace, and to losses to the atmosphere during the amendment procedure. Tubes were incubated at room temperature for 77 days, and during the incubation, they were shaken periodically to keep the medium oxygenated. At the end of the incubation, tubes were scored for growth (culture turbidity) by visual inspection, and an MPN of benzene-toluene degraders was determined from the appropriate 3-tube MPN table (Mayou, 1976).

3.3.2 Microbial Dehydrogenase Activity.

The electron transport system (ETS) test developed by Trevors et al. (1982) provides a direct measure of microbial activity in the aquifer material under specific incubation conditions. This test measures the activity of dehydrogenase enzymes associated with the electron transport system. The assay is based on the reduction of water-soluble 2-(*p*-iodophenyl)-3-(*p*-nitrophenyl)-5-phenyl chloride (INT) by dehydrogenase enzyme activity to methanol-extractable red iodonitrotetrazolium formazan (INT-formazan). Experiments were run to compare activities between different sample locations (pristine vs. contaminated) under similar substrate conditions, and between different substrate conditions for the same sample location.

Ten grams (wet weight) of aquifer material were incubated in crimp-sealed 60 ml hypovials. Active, blank and sterile control treatments were included in each experiment. Active treatments received 1 ml of 0.4% (w/v) sterile INT solution, one or more carbon sources (gasoline-saturated water, 1/10 gasoline-saturated water, or sterile 0.2% (w/v) glucose solution), nutrients (5 mg/L as N and 2 mg/L as P), and sterile distilled water, as required, so that each flask or vial received a total of 2.5 ml liquid. Sterile controls contained aquifer material that had been autoclaved for 1/2 hr on three consecutive days, and received 0.5 ml of 10% (w/v) sodium azide solution in place of sterile water. Blank treatments received water in place of INT solution. Each treatment was prepared in duplicate. Experiments were performed under aerobic conditions.

Flasks were sampled several times over ca. a 30 day incubation period by removing approximately 1 g of sand slurry, extracting the slurry with 5 ml methanol, and measuring the INT-formazan content spectrophotometrically (Trevors et al., 1982). An INT-formazan standard curve was generated using standards consisting of reagent INT-formazan in methanol. Blank-corrected INT-formazan content was reported on a dry weight basis.

3.4 Borden Field Experiment

3.4.1 Instrumentation

The field experiments were performed within 2m by 2m by 3.5m deep Waterloo Barrier™ sealable, sheet-piling cells. Cells were installed by vibrating the individual sections of sheet piling to the target depth. The joints were then sealed with bentonite grout to isolate the interior of the cell from the surrounding aquifer. The base of the cell was open to the underlying aquifer.

Each of the two treatment cells (i.e., Nitrate Cell and Control Cell) contained instrumentation for groundwater sampling, water-level measurements, gasoline injection, dewatering, geophysical measurements, and the addition and extraction of water. Cell instrumentation is shown on Figure 3-1. Most instrumentation was installed by advancing a steel casing to depth, washing the cuttings from the inside of the casing with flowing water, lowering the instrument, and then removing the steel casing. The formation was then allowed to collapse into the annular space. Drive points were vibrated into the ground using a pneumatic hammer.

Treatment Cells

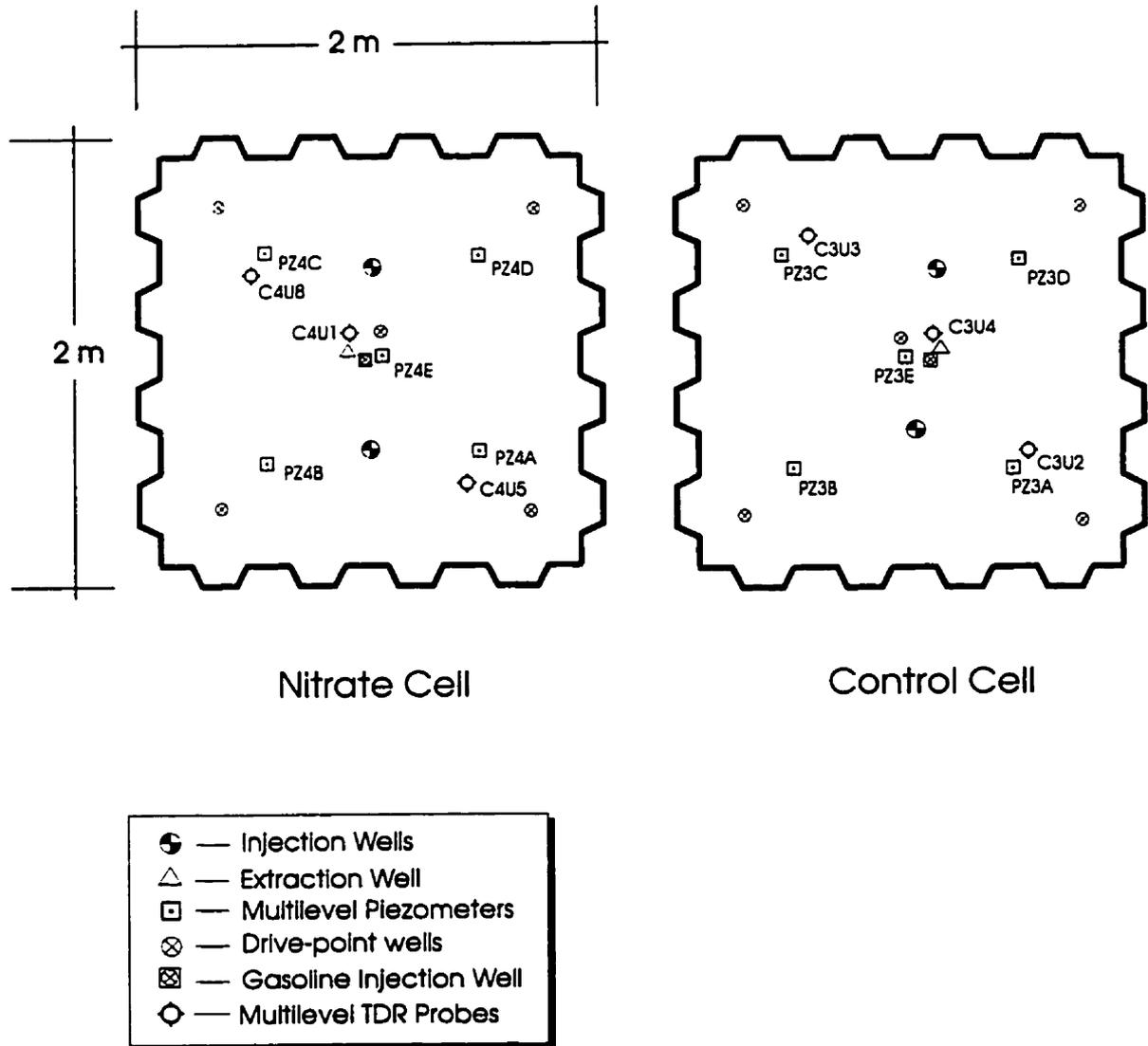


Figure 3-1. Plan view of treatment cells with surveyed locations of instrumentation.

The five multilevel piezometers in each cell were constructed of a series of 3.2 mm (1/8 in) stainless-steel tubes soldered to a 2.54 cm (1 in) stainless-steel center tube. Each piezometer had nine sampling ports, spaced 30 cm apart, between 30 and 270 cm bgs (below ground surface of cell). To avoid creating a preferential vertical flow path along the piezometer wall, the 3.2 mm tubes were placed inside the 2.54 cm center tube so that sample ports were flush with the center tube outside wall. Each cell contained five 2.86 cm (1-1/8 in) diameter stainless-steel drive point piezometers (depth 2.4 m; screen length 18 cm), used primarily for water level measurements. Each cell also contained three access tubes for geophysical measurements. The access tubes were constructed of 5.08 cm (2 in) diameter Schedule 40 PVC pipes (2.4 m depth) with solid 3.2 mm (1/8 in) stainless-steel rods embedded into the outside of the pipe. The rods were used to measure water content prior to the gasoline spill with time domain reflectometry (TDR).

To flush water vertically through the cells, both injection and extraction wells were also installed. Extraction wells were constructed of 2.86 cm (1-1/8 in) diameter stainless steel tubing flush-soldered to a 50-cm long drive-point screen; tops of screens were located 200 cm bgs. One centrally-located well was used in each cell for extraction of water (Figure 3-1). Water was injected into a high hydraulic conductivity layer located near the top of each cell. This layer was used as a means of distributing injected water horizontally without the use of multiple injection wells. It was installed by excavating the cells to ca. 60 cm, levelling the surface, and then backfilling with 8 cm of coarse sand, followed by 8 cm of 0.95 cm (3/8 in) diameter pea gravel. A commercial filter fabric was then placed over the pea gravel and the cells backfilled with 5 cm of coarse sand followed by native Borden sand to surface. Prior to backfilling, a 5.08 cm (2 in) PVC injection well with a 30.5 cm (12 in) well screen was installed in each cell to a 65-cm depth so that the screened interval straddled the pea gravel layer. Both of these PVC wells gradually lost transmitting capacity over the first 3.5 months of the experiment, and were replaced by stainless-steel drive point wells with No. 10 slot well screens, which operated for the remainder of the experiment (Figure 3-1).

A centrally-located drive-point gasoline injection well (depth 150 cm bgs; screen length 18 cm) and a 1.9 cm (3/4 in) diameter PVC dewatering well (depth 250 cm bgs; screen length 86 cm) were also installed in each cell (for clarity not shown on figure).

After the equipment was installed, plastic tarps were placed on the surfaces of the cells as vapor barriers. Gaps around well casings were sealed with roofing tar or silicone. These sealants were not in contact with injected water or gasoline. The outer edges of the cells were sealed by packing a wedge of thick bentonite grout along the crenulated wall of the sheet piling. The grout was then covered with sand to slow desiccation. A monitoring and pumping-well network was also installed downgradient of the cells to detect releases and control the plume, if necessary (Figure 3-2). Periodic sampling of downgradient multilevel piezometers indicated that gasoline releases did not occur (Appendix D). To prevent infiltration of rainwater, a greenhouse was constructed over the cells.

3.4.2 Gasoline Injection

The objective of the spills was to emplace a source of gasoline below the water table as a spatially-uniform, residual phase so that abiotic losses (volatilization, physical removal during high water-table events) and preferential flow of water around gasoline-contaminated zones would be minimized. To emplace the sources, the water table was lowered, the gasoline gravity-fed into the gasoline injection wells, and the water table allowed to recover to the pre-spill elevation.

Seventy liters of API 91-01 gasoline (Appendix A) were injected into each cell during October, 1995. Prior to injection, the ambient water table was approximately 70 cm bgs. The water table was lowered using pumps connected to the four corner drive point wells, and the PVC dewatering well. The Control Cell was dewatered for 29 hrs and the Nitrate Cell for 47 hours prior to injection (injections occurred on successive days). In both instances target water-table depths (Nitrate Cell: 175 cm bgs; Control Cell: 180 cm bgs) were reached and maintained for several hours prior to gasoline injection to give the moisture content profile time to respond to the falling water table and approach a condition of static equilibrium. The target water table depth was chosen so that the top of the capillary fringe would be roughly coincident with the base of the gasoline injection well. The thickness of the capillary fringe is about 30 cm in the Borden aquifer (Nwankwor et al., 1992). Water-content profiles collected with the multilevel TDR probes 1-3 hrs before injection show that the top of the capillary fringe was slightly higher than anticipated in both cells (Figure 3-3). A description of the methods used to collect and process the TDR data is provided by Oliveira (1997).

Site Plan

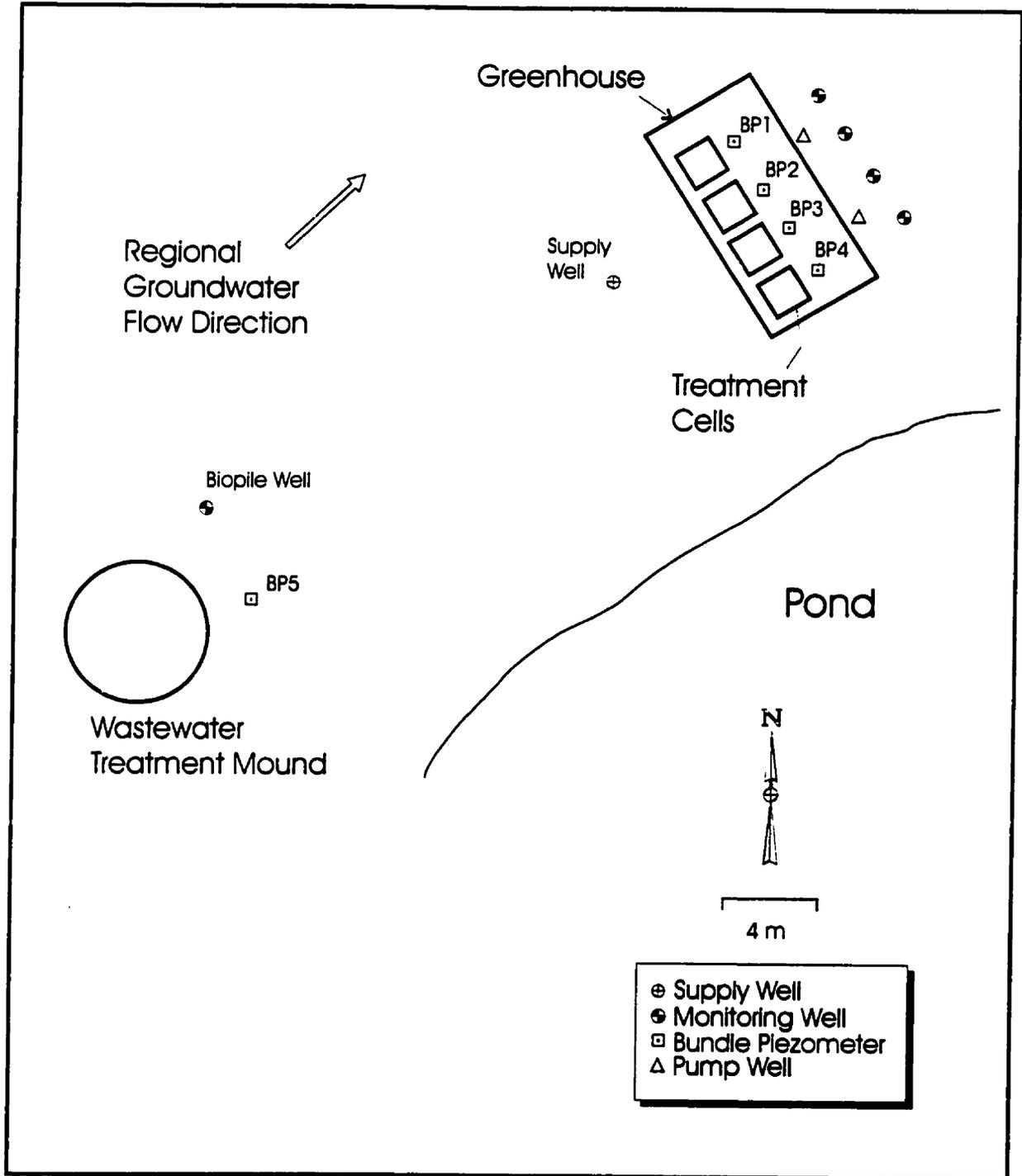


Figure 3-2. Plan view of study area.

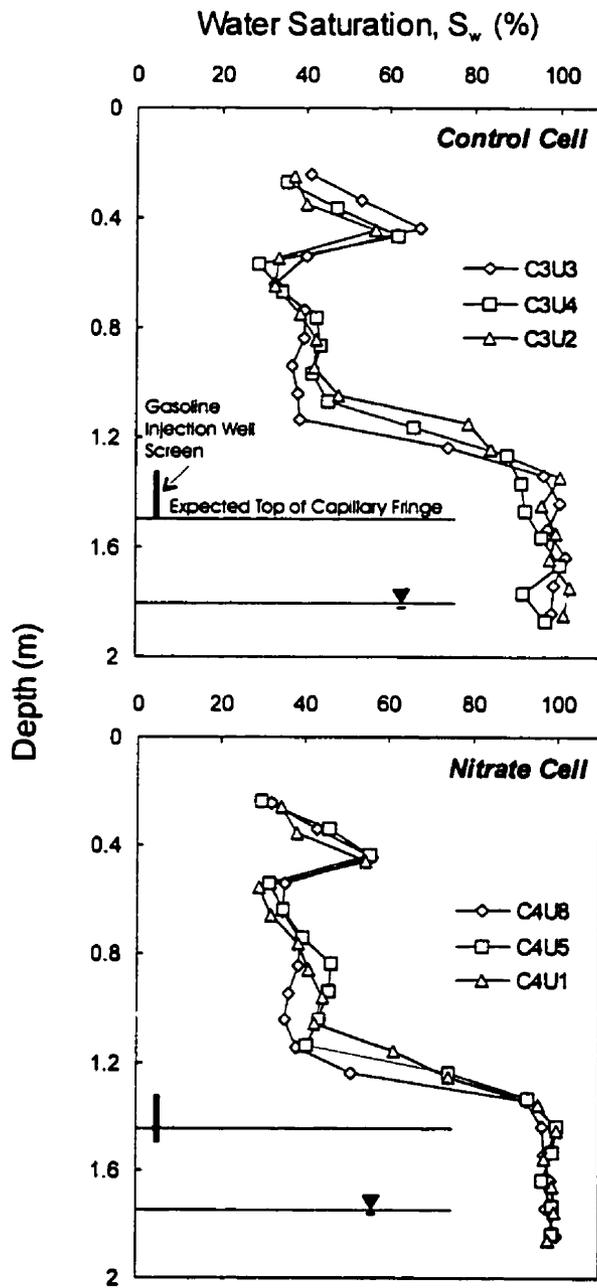


Figure 3-3. Vertical profiles of water saturation prior to the gasoline injections. Profiles were obtained 1-3 hours before injection with multilevel TDR probes.

Gasoline was gravity-fed into the gasoline injection wells from a sealed, polyethylene tank. The durations of the injections were 5 hr 45 min for the Nitrate Cell, and 7 hr 45 min for the Control Cell. A partially-clogged flow meter was responsible for the slower rate of injection into the Control Cell. Groundwater extraction from the center drive-point well (screen depth 222-240 cm bgs) continued throughout the injection. However, these wells were incapable of sustaining the required extraction rate, and the water table rose ca. 10 cm in both cells during the injections. Extraction wells were turned off immediately after the injection of gasoline was completed. After about two weeks, the water table had recovered to pre-injection levels. Because the injection procedure involved dewatering, a trapped air phase was probably also present below the water table. The mass of O₂ in the trapped air phase was estimated and incorporated into mass balance calculations (Appendix E). The extent of volatilization that occurred during gasoline injection could not be quantified, but based on relatively short contact times with the atmosphere during injection and analysis of groundwater from gasoline-contaminated zones one month after injection (see below), volatilization losses of target compounds appeared minor.

Detailed measurement of the *in situ* magnitude and structure of the trapped gasoline and air phases was considered beyond the scope of the research. A detailed characterization of their distribution was therefore not attempted, but a general understanding of the distribution of the injected gasoline was developed from field observations, groundwater samples, and core-extract data. The distribution of aqueous-phase BTEXTMB concentrations during November, 1995, one month after injection, is shown in Figures 3-4 and 3-5. These figures suggest that the gasoline phase did spread radially outward from injection wells as intended, and was present mainly in the 120 cm to 60 cm bgs depth interval. The gasoline contaminated zones were thickest in the vicinity of the injection wells, extending to a depth of approximately 150 cm bgs. These initial observations were confirmed by the results of the post-experiment coring (Chapter 5). However, complete trapping below the water table apparently did not occur; after recovery to the pre-injection head, a thin layer of gasoline was observed on the water table in the Control Cell. This indicated that the 110 cm recovery following injection did not trap all of the gasoline below the water table. During the November sampling round, it was also observed that a mobile gasoline phase was present near some of the sampling ports; some samples contained a gasoline/water mixture, as indicated by field observations and concentrations well above those in gasoline-saturated water (Figures 3-4 and 3-5). Overall, however, the injections were successful in

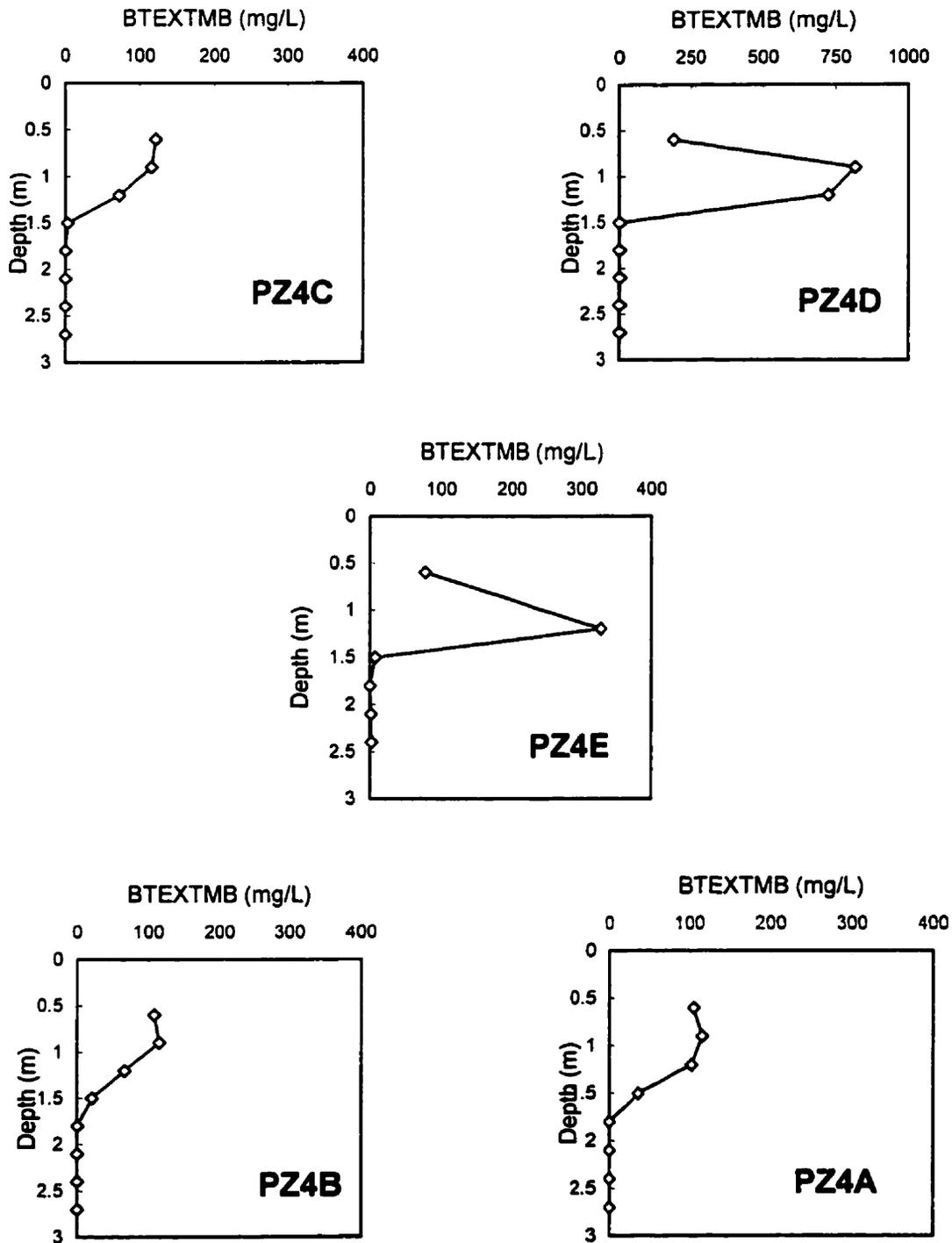


Figure 3-4. Vertical profiles of total dissolved BTEXTMB in the Nitrate Cell on November 22-26, 1995, approximately one month after gasoline injection. The water table depth was approximately 50 cm bgs. Note scale change for piezometer PZ4D.

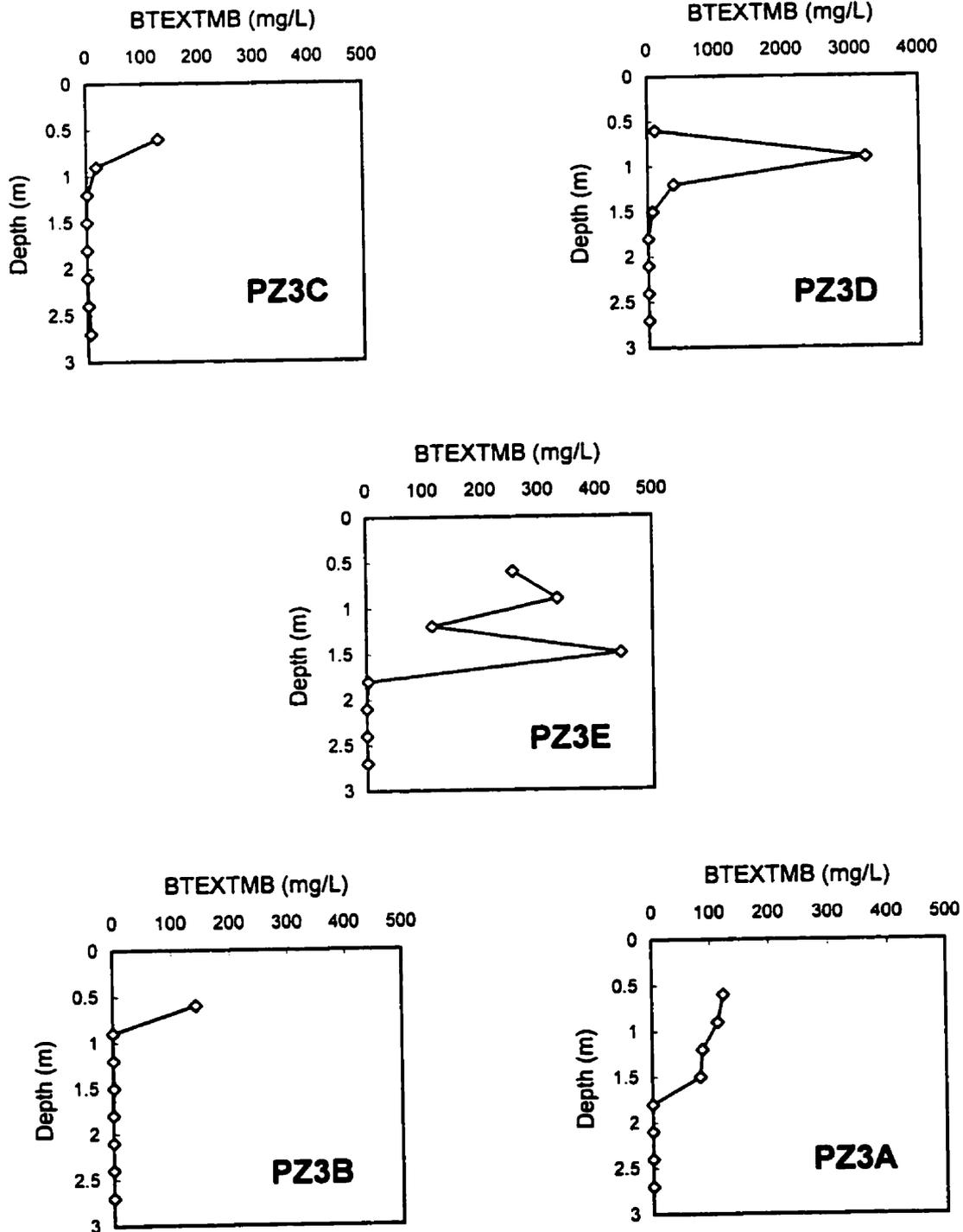


Figure 3-5. Vertical profiles of total dissolved BTEXTMB in the Control Cell on November 22-26, 1995, approximately one month after gasoline injection. The water table depth was approximately 50 cm bgs. Note scale change for piezometer PZ3D.

emplacing a source below the water table, and the gasoline distributions were suitable for meeting the goals of the experiment.

During the following Spring snowmelt, groundwater with a sheen of gasoline was observed above the surfaces of the cells. The amount of gasoline removed from the cells during this event could not be determined, but visual observations and samples of the standing water suggested that losses were minor (data not shown). In addition, the high water table may have trapped some gasoline above the gasoline-contaminated zone contacted by amended water during the flushing experiments. These regions were cored at the end of the experiment and any mass that was present was included in mass balance calculations. As shown in Chapter 5, the amount of gasoline above the pea-gravel layer appeared relatively minor.

3.4.3 Experimental Design

Injection Procedures. To obtain data that could be used for a mass balance, injection systems were designed to flush water continuously through the cells at a constant flux. A schematic of the injection system is shown in Figure 3-6. A vertically-downward flow field was created by injecting into the pea gravel layer (50 cm bgs), and extracting from the extraction well (screen: 200-250 cm bgs) (Figure 3-6). The length of the vertical flowpath was therefore about 1.75 m. Constant lower head conditions were maintained by water level controllers (SSAC Inc., LLC5 Series) which automatically cycled the extraction pumps on and off. The injection pumps operated continuously. By adjusting the elevation of the lower heads, upper heads in both cells were maintained at about 50 cm bgs under constant injection conditions, despite fluctuating water table elevations in the aquifer.

During the first week of the experiment, water was obtained from a shallow upgradient well located in a flooded area. This well appeared to be pumping surface water which was fully oxygenated. To obtain groundwater with lower dissolved O₂, a shallow PVC well (2.49 m total depth) located approximately 6 m upgradient of the cells was used as the water supply for the remainder of the experiment (Figure 3-2). To inject the same dissolved oxygen concentration into both cells, a single 0.635 cm (1/4 in) diameter polyethylene tube was installed in the well as the intake line. This line was then split with a Y-connector, and lines were run to individual injection

Injection System

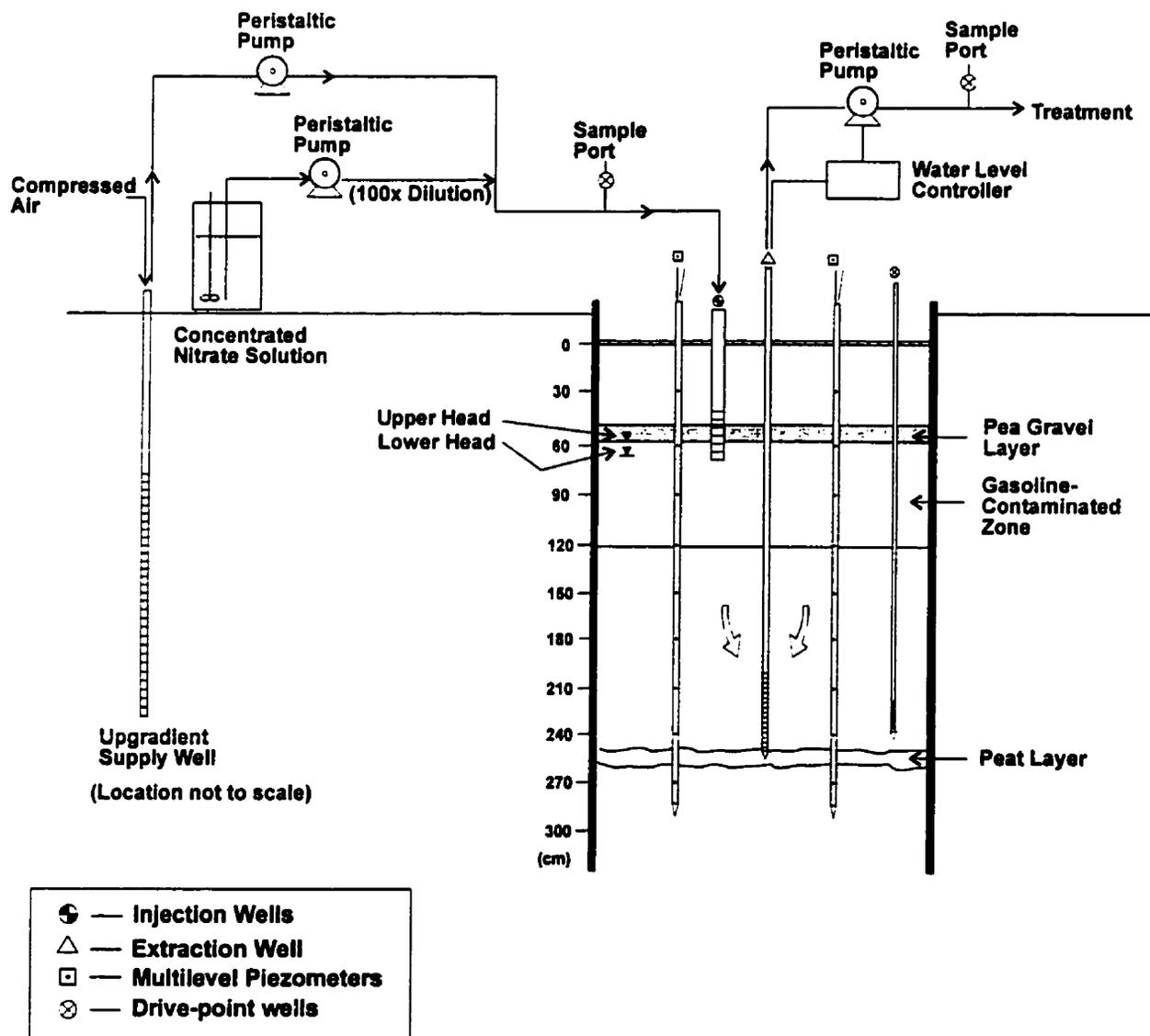


Figure 3-6. Injection system schematic for the Nitrate Cell. Cross section of cell shows selected instrumentation to illustrate positions of injection/extraction wells and multilevel piezometer ports. The system for the Control Cell was identical except for NO_3^- addition equipment.

peristaltic pumps (Masterflex L/S Series). The Control Cell received no additional amendments prior to injection; the Nitrate Cell received NO_3^- via a Swagelok® fitting located downstream of the injection pump.

Dissolved O_2 concentrations were controlled by placing an aerator tube in the supply well. The aerator was located just above the water intake tube to minimize incorporation of bubbles. The target dissolved O_2 concentration range was 2-4 mg/L. This arrangement provided reasonable control over dissolved O_2 concentrations, but also appeared to stimulate growth of unidentified bacteria (possibly Fe oxidizers) in the supply well, injection tubing, and injection wells. During the final 24-day flushing experiment (May 1997), the injected dissolved O_2 concentration was increased to ca. 5 mg/L by switching the water supply from groundwater to the pond adjacent to the site.

The injection NO_3^- concentration was controlled by pumping a continuously-stirred, concentrated NO_3^- stock solution into the injection flow line. A dedicated peristaltic pump (Masterflex L/S Series) was used to feed stock solution into the line. The pumping rate was set to yield a 100x dilution. The stock tank held 40 L of solution and was replenished every two weeks. The initial target injection concentration was 150 mg/L NO_3^- , but because utilization was low, the target concentration was lowered to 100 mg/L on day 67. During the 24-day flushing experiment, the possibility that microbial activity was nutrient-limited was investigated by pumping a modified Bushnell-Haas (MBH) medium (K_2HPO_4 at 2 g/L; KH_2PO_4 at 2 g/L; NH_4NO_3 at 2 g/L; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ at 0.4 g/L; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at 0.04 g/L; $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 0.01 g/L) (Mueller et al., 1991) into both cells using a concentrated stock solution and dedicated feed-pump as above. The dilution rate was 100x. Because of pump malfunctions, the solution was pumped in intermittently over the 24 day period. Actual injected concentrations are not known because complete dissolution of the concentrated stock solution could not be maintained.

Injection flow rates were set by calibrating the peristaltic pump controllers, and measured periodically (n=22) using a stopwatch and graduated cylinder. During the first two months of the experiment, target flow rates were adjusted periodically to achieve steady flow conditions and the desired residence time. Target flow rates and actual measurements are shown on Figure 3-7. To calculate a mean flow rate representative of the entire 174-day flushing experiment, a mean and

Injection Rates

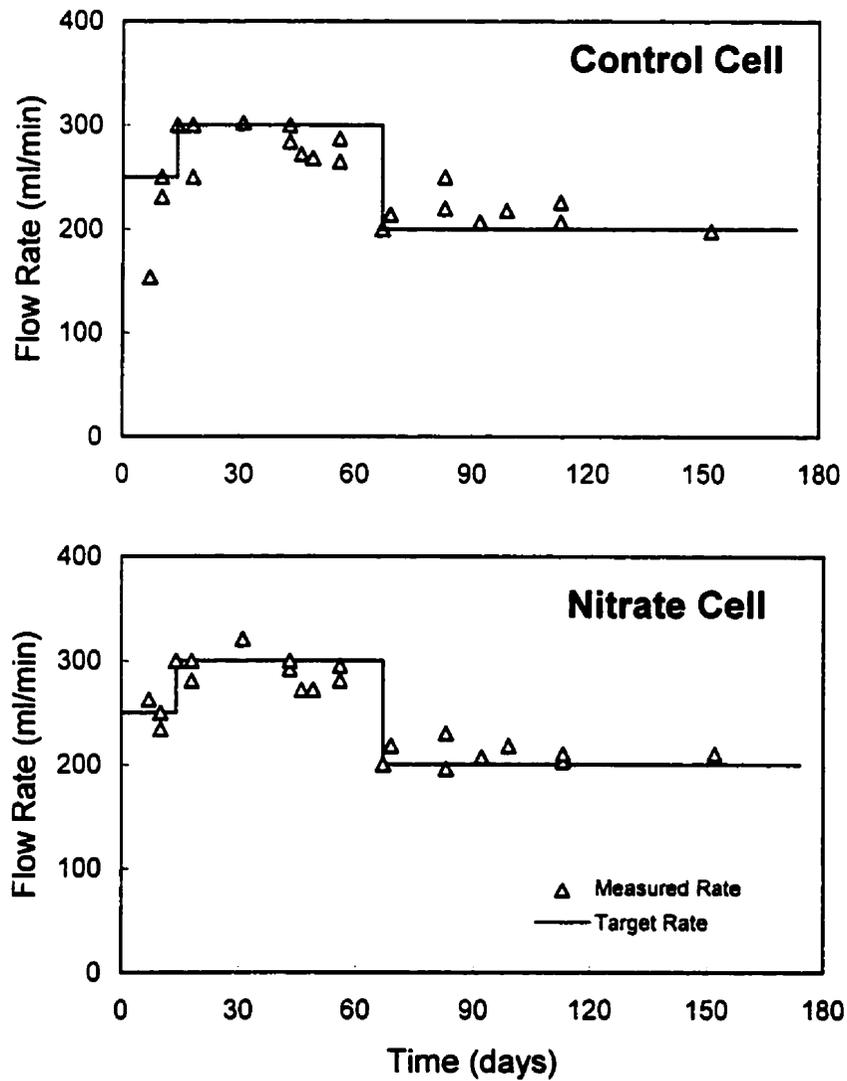


Figure 3-7. Record of injection rates over the 174-day flushing experiment.

standard deviation were calculated for each of the three target injection-rate periods (Figure 3-7). An overall mean was then calculated from the individual mean injection rates, and a pooled standard deviation from the individual standard deviations. These calculations yielded rates of 250 ± 14 ml/min and 237 ± 23 ml/min for the Nitrate and Control cells, respectively. The uncertainty is the standard deviation of the temporal distribution of injection rates. These injection rates correspond to residence times of about 9 days, or 20 treatment-cell pore volumes over 174 days. On the basis of a measured rate of 200 ml/min ($n=1$), an additional three pore volumes were removed from each cell during the 24-day flushing period the following spring.

Peristaltic pumps (Masterflex L/S Series) were also used to extract groundwater. Extracted groundwater was pumped into a polyethylene holding tank, and then to an unsaturated soil mound located 30 m upgradient of the treatment cells (Figure 3-2). In previous studies at Borden, infiltration through the unsaturated zone was shown to be an effective means of stimulating aerobic biotransformation of aromatic hydrocarbons (O'Leary et al., 1995). The absence of detectable BTEXTMB in a downgradient multilevel piezometer and well showed that infiltration through the mound effectively attenuated these compounds (Appendix D).

To operate continuously the injection system required regular maintenance, mainly pump tubing replacement and injection/extraction well cleaning. The 1/4-in tubing that transported water between the supply well to the injection wells was also replaced on a regular basis. During the first few months of the experiment, unanticipated problems such as power outages led to several shutdowns on the order of 24 hours duration. Routine maintenance, however, required the injection systems to be shut off a few times a week for only 1 hour.

Tracer Test. During July, 1996, tracer tests were performed in both treatment cells (Appendix B). The main objectives of the test were to confirm that the injected water was distributed uniformly in the cells (i.e., minimal short-circuiting), and to calculate dispersivities and linear groundwater flow velocities.

3.4.4 Field Sample Collection

Groundwater Samples. Transport of aqueous organics and added electron acceptors was monitored by routine sampling for BTEXTMB, dissolved O₂, NO₃⁻, and NO₂⁻. Samples were collected biweekly from the five piezometer ports at the 60 cm bgs and 180 bgs depths. Monthly vertical profiles from the center piezometers were also determined. Changes in geochemical conditions were determined by less-frequent analysis of one or more of the following: pH, temperature, alkalinity, Fe, sulfate (SO₄²⁻), HS⁻, and CH₄.

Groundwater samples were collected from the small piezometer tubes with a peristaltic pump. BTEXTMB samples were collected in 18-ml crimp-top glass vials clamped onto an in-line stainless-steel sampling head (Figure 3-8). Previous tests indicated that there was no significant bias introduced by this sampling procedure (Barker et al., 1987). In this experiment cross-contamination between sampling ports was minimized by proceeding from low-concentration to high concentration locations, and cleaning the sampling head with acetone and distilled water after sampling highly-contaminated ports. In addition, because the 18-ml vial remained in-line while the D.O. and inorganic samples were collected, a minimum of 100 ml of groundwater were flushed through the system prior to obtaining an organics sample. Blanks collected periodically by flushing organic-free distilled water through the sampling apparatus confirmed that cross-contamination was negligible (Appendix F). Each BTEXTMB sample was preserved with 0.1 ml of 10% (w/v) sodium azide solution, sealed without headspace with a Teflon-faced septum and aluminum crimp seal. Samples were refrigerated until analysis, which typically occurred within 3 days of collection.

After pumping ca. 25 ml of water to flush the piezometer tubes of stagnant water, dissolved O₂ concentrations were measured colorimetrically in the field (indigo-carmin method (Gilbert et al., 1982)). Samples were collected under low-flow conditions from a flow-through sample cup attached to the end of the peristaltic-pump outlet tube (Figure 3-8). Samples were typically colorless, and free of turbidity. To obtain a sample, a CHEMetrics Vacu-Vial[®] O₂ ampoule was inserted in the flowing stream of water and filled. The concentration was read in a CHEMetrics VVR spectrophotometer, using a dedicated filter for the specific analyte and concentration range. Two O₂ filters were used in this study: a 0-15 mg/L range filter, and a 0-2 mg/L range filter. Each

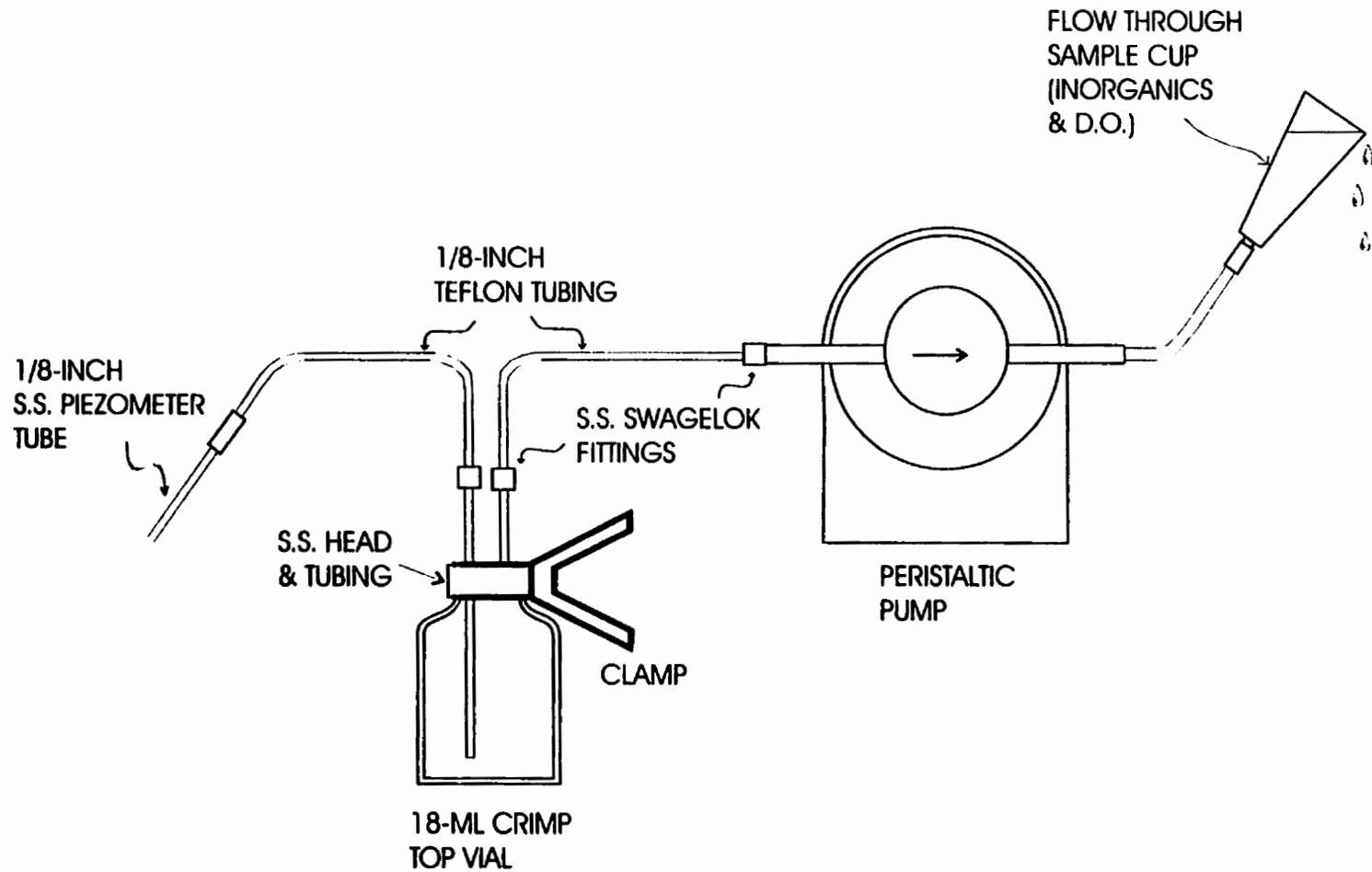


Figure 3-8. Schematic of groundwater sample collection apparatus. Dissolved O₂ samples collected from sample cup under flowing stream of water.

filter contained a pre-programmed calibration curve, and did not require daily calibration. The accuracy of the calibration was tested in the laboratory using air-sparged water (aerobic) and a 2% (w/v) sodium sulfite solution (O_2 -free). The ambient temperature of the laboratory was 24°C. This test yielded concentrations of 7.54 ± 0.18 mg/L ($n=5$) for the aerobic water, and 0.0 ± 0.0 ($n=5$) for the O_2 -free water. At this temperature the concentration of dissolved O_2 in equilibrium with air (one atmosphere total pressure) is 8.25 mg/L (Drever, 1982). The majority of the field samples were analyzed with the 0-2 mg/L range filter. The specified method detection limit (MDL) for this filter was 0.05 mg/L dissolved O_2 .

If required, samples for inorganic parameters were then collected from the outlet tube of the peristaltic pump (Figure 3-8). Nitrate samples were collected in 18-ml scintillation vials and preserved with two drops of formaldehyde. Iron and SO_4^{2-} samples were collected in 30-ml glass syringes and then filtered ($0.45 \mu m$) into scintillation vials. Samples for Fe analysis were acidified with 2-3 drops of concentrated hydrochloric acid. Groundwater samples for dissolved CH_4 analysis were collected without headspace in 40-ml screw-top glass vials. All of these samples were shipped back to the University of Waterloo for analysis (Appendix C).

Total dissolved sulfide concentrations were also measured in the field using a CHEMetrics colorimetric analysis (MDL=0.06 mg/L) in a manner similar to dissolved O_2 . Total alkalinity as $CaCO_3$ was measured in the field with a Hach Digital Titrator (Model 16900).

Injection/Extraction Samples. Concentrations of electron acceptors injected into the cells were determined by frequent (daily to bi-weekly) sampling of injection water for NO_3^- , NO_2^- , and dissolved O_2 . To provide a baseline, the injection stream was also sampled at least once for dissolved organic carbon (DOC), pH, temperature, alkalinity, Fe, SO_4^{2-} , HS^- , and BTEXTMB. Similarly, extraction water was analyzed regularly for NO_3^- , NO_2^- , dissolved O_2 , and BTEXTMB, and less frequently for the inorganic parameters listed above. Samples of injection water were collected directly from the end of the injection tubing, and extraction water from a sampling port (Figure 3-6). Collection procedures and preservatives were as described in the preceding paragraphs.

Metabolites. Evidence for biotransformation was obtained by analyzing samples for hydrocarbon metabolites. These compounds (aromatic and aliphatic acids and phenolic compounds) result from incomplete mineralization of various hydrocarbon constituents. Three sets of samples were collected, all under static conditions: May 1997, early June 1997, and late June 1997. The first two sets of samples were shipped to the National Center for Integrated Bioremediation (NCIBRD) at the University of Michigan, Ann Arbor for analysis, and the third to the U.S. EPA's National Risk Management Research Laboratory (NRMRL) in Ada, OK.

Samples were collected from two locations within each cell, and the groundwater supply well. A fresh sample of API 91-01 gasoline was also analyzed by NRMRL for these compounds. Samples were collected from the peristaltic pump outlet tube in 500 ml amber bottles, preserved with either KOH to pH=11 or 1% (w/v) trisodium phosphate solution, and refrigerated until shipment.

Aquifer Cores From Treatment Cells. When the field experiments were completed, cores were collected to estimate the mass of aromatic hydrocarbons remaining in the treatment cells. Core subsamples were immersed in solvent in the field immediately after collection to obtain an estimate of total contaminant mass in the aquifer sample, including mass in the sorbed, aqueous, and residual gasoline phases. For aquifers that have been exposed to low concentrations of organics for an extended period of time, the efficiency of the extraction, particularly of the sorbed phase, is critical for obtaining accurate results (Ball et al., 1997). In this experiment, on the other hand, there was a large absolute amount of mass (ca. 7 kg BTEXTMB recovered in each cell), and a high proportion of this mass was necessarily present within the gasoline phase; the sorbed and aqueous phases therefore contributed negligible mass to the total estimate. Moreover, the Borden aquifer material is composed predominantly of quartz sand (i.e., not likely to have substantial intraparticle porosity), and the extent of sorption is relatively low (Patrick et al., 1985). Consequently, a relatively-simple extraction procedure similar to Vandegrift and Kampbell (1988) was used in this study (see below).

Several days prior to coring, sample bottles (40-ml screw-top glass vials with TeflonTM-faced septa) were prepared by weighing the empty bottles, adding 15 ml methanol, and then reweighing the bottles to record the actual methanol mass. Bottles were then stored in the

refrigerator until needed. There were no samples with substantial (visible) losses of methanol over the time period that elapsed between bottle preparation and sample analysis.

Cores were extracted from the treatment cells using the procedures described in Section 3.1. Grids consisting of nine equal areas were used to determine core locations. One core was collected from the center of each area. An additional core was collected from a second location near the center of each cell. Core runs were typically from ground surface to 152 cm (5 ft) with recoveries averaging 117 cm and 124 cm from the Control and Nitrate cells, respectively. A deeper interval, 152 cm to 305 cm (5 to 10 ft), was also obtained from the cores at cell centers (cores 3J and 4K). Complete core recoveries were not obtained. When cores were brought to the surface, the lower end was immediately sealed with a plastic cap. The empty, upper part of the core tube was then cut off prior to removing the piston, and the upper end of the full core tube capped. As discussed in greater detail in Appendix E, it was assumed for mass-balance calculations that incomplete core recovery did not result from compaction. Consequently, subsample depths were not adjusted for incomplete recovery. For most cores eight uniformly-spaced subsamples were collected, corresponding to one subsample per 15-cm interval. Mass balance calculations were therefore based on approximately 80 samples per cell.

Subsamples of aquifer material were collected within 15 minutes of core extraction. To obtain these samples, a 2-cm wide strip of the core barrel was removed with a circular saw to expose the aquifer material. At each sampling location the outer layer of sand was scraped away, and a plug of sand (approximately 10-g) was obtained by inserting the barrel of a dedicated, plastic 10-cc syringe into the core. The plug of sand was then quickly extruded into a preweighed sample bottle, recapped, and refrigerated on-site. Core subsamples were collected over a two-day period, and transported at the end of the second day to the University of Waterloo where they were stored at 4°C. Bottles were weighed again in the laboratory to determine the wet weight of the aquifer sample. Six days after collection, samples were shaken for 15 min at 300 rpm on an orbital shaker to enhance extraction, and then sonicated for 3 min to remove any emulsification that may have been present in the methanol. On the basis of a visual inspection, all samples were composed of clean Borden sand with no evidence of significant soil aggregation; during shaking samples formed a uniform slurry in the methanol phase suggesting good contact between phases. Sample

analysis began approximately one week after this procedure. The analytical method is described in Section C.2.

To estimate the extent of depletion of other gasoline constituents, a total of six additional subsamples of core material were collected from randomly-selected locations within the 20 cores collected from the cells for a semiquantitative analysis of gasoline components (i.e., grouped as alkanes, aromatics, bicycloalkanes, naphthenes, olefins, and PNAs) at the NRMRL in Ada, OK. The core subsamples were extruded into 40-ml screw-top glass vials containing 25-ml deionized water and refrigerated until shipment to the NRMRL for analysis. For comparison, fresh API 91-01 gasoline and an aliquot of Borden sand spiked with API 91-01 were also analyzed for these component groups. Details of the analytical method are provided elsewhere (Hutchins et al., 1998).

Following core collection, a Quality-Assurance/Quality-Control test was performed in the laboratory to assess gasoline recovery efficiencies using the methanol-extraction procedures described above. A detailed description of the test is included in Appendix F. In brief, a known mass of API 91-01 was spiked into 40-ml vials containing known amounts of methanol (15 ml) and Borden aquifer material (10 g). Samples were then handled as described above for the field samples (e.g., 14-day storage period), and quantified using fresh standards prepared from the gasoline on the day of analysis. Methanol blanks and gasoline standards were also stored and extracted with the aquifer samples. Gasoline was spiked into pristine aquifer material (n=5), and contaminated aquifer material from three locations in the Nitrate Cell (n=5 replicates per location). For each of the contaminated locations, a set of unspiked replicates (n=5) was also prepared and extracted to determine the background aromatic-hydrocarbon concentrations. For these samples, spike recoveries were determined by first subtracting off the mean background concentration of each constituent. A summary of mean percent recoveries is shown in Table 3-2. Percent recoveries ranged from a low of 79% to 113%. The results generally indicated that the extraction procedure was adequate for this aquifer material, but for most compounds the procedures used here may have imposed a minor negative bias on the estimates of residual mass in the treatment cells. These issues are discussed further in Appendix E.

Table 3-2. Results of API 91-01 spike test to evaluate aromatic-hydrocarbon recovery efficiencies in core-extract samples.

Compound	Mean % Recovery			
	Pristine Core	Contaminated Core		
		Core 2-2	Core 4M	Core 4O
Benzene	90.9	91.7	85.6	79.4
Toluene	88.0	87.9	81.5	81.7
Ethylbenzene	89.0	88.8	80.6	83.8
<i>m+p</i> -Xylene	90.3	90.3	81.6	85.4
<i>o</i> -Xylene	92.5	93.1	83.6	88.1
1,3,5-Trimethylbenzene	101.3	101.6	90.4	97.4
1,2,4-Trimethylbenzene	99.1	100.3	85.2	95.4
1,2,3-Trimethylbenzene	102.6	103.6	94.1	100.0
Naphthalene	106.6	113.5	105.4	108.3

See Appendix F for aromatic-hydrocarbon concentrations and % relative standard deviations of replicate means.

CHAPTER 4. LABORATORY EXPERIMENTS

Section 4.1 includes the microcosm experiments performed with pristine Borden sand. Experiments 1 and 2 were set up after the field experiment was designed and the gasoline spilled, but before electron-acceptor flushing was initiated. Section 4.2 includes the follow-up microcosm experiment performed with contaminated aquifer material collected from the Nitrate Cell. Section 4.3 contains the results of all of the microbiological characterization work performed over the course of this study. The major conclusions from all of the microcosm experiments and microbiological characterization studies are summarized in Table 4-1.

Except where noted in Section 4.2, it was assumed that NO_3^- was utilized primarily as an electron acceptor under anaerobic conditions. This assumption is consistent with previous laboratory studies in which Borden aquifer material was amended with aromatic hydrocarbons and NO_3^- , and denitrification was confirmed with an assay (Major et al., 1988; Barbaro et al., 1992). The term "denitrifying activity" is used here in a general sense to define any dissimilatory NO_3^- -reducing activity occurring under anaerobic conditions. The term "denitrification" is only used when an assay was performed to confirm that NO_3^- was reduced to gaseous end products. In this study substrate and electron-acceptor disappearance curves were used as indicators of mass loss in laboratory microcosms. Substrate mineralization could not be verified because CO_2 evolution was not monitored.

4.1 Microcosm Experiments: Pristine Borden Sand

Hydrocarbon-contaminated aquifer material from an existing spill in the Borden aquifer was not available for preliminary laboratory experiments. Thus the experiments that provided baseline information on electron-acceptor and aromatic-hydrocarbon utilization under highly-contaminated conditions were performed with aquifer material that had no known prior exposure to hydrocarbon contamination. The microbial community in a low-carbon environment such as the Borden aquifer may require time to adapt to the unfavorable conditions created by a hydrocarbon spill (Chapelle, 1993). Adaptation is the result of changes such as enzyme induction, genetic mutation, or selective enrichment and growth of organisms capable of degrading

hydrocarbons (Leahy and Colwell, 1990; Chapelle, 1993). It was anticipated that the hydrocarbon-degrading abilities of contaminated aquifer material would increase with length of exposure. This provided an opportunity to compare aromatic-hydrocarbon and electron-acceptor utilization in pristine and contaminated Borden sand for evidence of adaptation to the hydrocarbon contamination.

Table 4-1. Summary of major conclusions from laboratory experiments.

Thesis Section	Experiment	Major Conclusions
4.1.1	Effect of substrate concentration under microaerophilic / NO_3^- conditions in pristine Borden aquifer material (Experiment 1)	Very minor BTEXTMB losses at gasoline-saturated aqueous concentrations, likely at the expense of microaerophilic O_2 ; patterns of NO_3^- utilization suggested denitrifying population in pristine material inhibited by high substrate concentrations
4.1.2	Effect of O_2 concentration under high substrate concentration conditions in pristine Borden aquifer material (Experiment 2)	Aerobic biotransformation at gasoline-saturated aqueous concentrations highly variable in pristine aquifer material; may indicate patchy distribution of aerobic populations tolerant of high substrate concentrations

Thesis Section	Experiment	Major Conclusions
4.2.1	Extent of biotransformation under various substrate and mixed electron-acceptor conditions in gasoline-contaminated Borden aquifer material extracted from Nitrate Cell (Experiment 3)	Large O ₂ demand and BTEXTMB mass loss relative to pristine aquifer material; nitrate possibly used as N source during aerobic degradation; relatively rapid continued NO ₃ ⁻ utilization following O ₂ depletion, but no discernable utilization of aromatics; differences between pristine and contaminated aquifer material suggested adaptation had occurred with large O ₂ demand in the latter; minor mass losses under microaerophilic / NO ₃ ⁻ conditions consistent with <i>in situ</i> observations
4.3.1 and 4.3.2	Microbial characterization results	Numbers of culturable aerobic heterotrophs and denitrifiers in Borden aquifer variable but consistent with other pristine shallow aquifers; after 19 month exposure, microbial numbers in treatment cells slightly elevated relative to pristine background locations; ETS activity generally greater in contaminated samples; activity assay also suggested that microbial activity was suppressed by gasoline phase

4.1.1 Microcosm Experiment 1

This experiment was performed because it became evident after the gasoline spills were completed that the entire volume of the treatment cells would be exposed to pure-phase gasoline and/or high aqueous concentrations of the soluble aromatic hydrocarbons. A microcosm experiment was therefore designed to evaluate the effects of aqueous concentrations on the extent of biotransformation under conditions similar to the field, i.e., gasoline-saturated groundwater plus NO_3^- and microaerophilic O_2 .

Microcosms were prepared with pristine Borden sand from cores collected near the field site. A 2-ml air headspace was present in each vial to create microaerophilic conditions. Three treatment groups were used to evaluate the effect of substrate concentration: high-BTEXTMB concentration (gasoline-saturated groundwater), low-BTEXTMB concentration (10x dilution of gasoline-saturated groundwater), and low-BTEXTMB-concentration sterile controls. For each treatment group replicate microcosms were sampled on days 0, 42, and 137 for BTEXTMB, dissolved O_2 (modified Winkler method), NO_3^- , and NO_2^- . Unfortunately, the O_2 concentrations in the control microcosms appeared anomalous, possibly from interferences between the Winkler reagents and the sodium azide. Subsequent controls analyzed with the dissolved O_2 meter indicated that the initial dissolved O_2 concentration in microcosms with a 2-ml air headspace was about 5 mg/L, declining asymptotically to below 1 mg/L over a four-month period (see Section 4.2.1; Figure 4-4). The design is summarized in Table 4-2.

This experiment was designed so that the differences between the means of the treatment groups could be evaluated with a statistical test. Because substantial variability in the extent of biotransformation is often encountered in microcosms that contain Borden sand, a large number of replicates was prepared for each treatment group to give the test reasonable power to detect differences. However, as observed in previous microcosm experiments with a day 0 sampling event (Unpublished Data), concentrations behaved anomalously, increasing between days 0 and 42, which prevented a statistical analysis of the mass-loss data.

Table 4-2. Design summary, Experiment 1.

Treatment (Initial BTEXTMB Concentration)	Replicates	Sampling Events
Active, 110 mg/L BTEXTMB (gas.-sat. water), 2-ml air headspace, 25 mg/L NO ₃ ⁻ -N, N,P	8 active	3
Active, 11 mg/L BTEXTMB (10x dil.), 2-ml air headspace, 25 mg/L NO ₃ ⁻ -N, N,P	8 active	3
Sterile, 11 mg/L BTEXTMB (10x dil.), 2-ml air headspace, 25 mg/L NO ₃ ⁻ -N, N,P	8 sterile	3

Results. Aromatic-hydrocarbon losses were not evident over 137 days of incubation in the high-substrate-concentration or sterile-control microcosms (Figure 4-1). On the other hand, mass losses were observed in the low-substrate-concentration microcosms (Figure 4-1). In terms of individual compounds, toluene, ethylbenzene, *m+p* xylenes, 1,2,4-trimethylbenzene, and naphthalene concentrations all declined relative to sterile controls by day 137 (Table 4-3). The remaining aromatic hydrocarbons appeared recalcitrant; the slightly lower concentrations shown on Table 4-3 may be attributed to aerobic biotransformation, to greater sorption in the active microcosms relative to the autoclaved controls, or a combination of the two processes.

By day 42, O₂ was depleted to a threshold concentration in the aqueous phases of both active treatments. Assuming initial concentrations in the active microcosms were similar to aqueous sterile controls (i.e., 5 mg/L), roughly half of the dissolved O₂ was consumed within the first several hours of the experiment (Figure 4-1). Nitrate also declined in the low-substrate-concentration microcosms relative to the sterile-control and high-substrate-concentration microcosms, but an accumulation of detectable concentrations of NO₂⁻ did not occur (Figure 4-1).

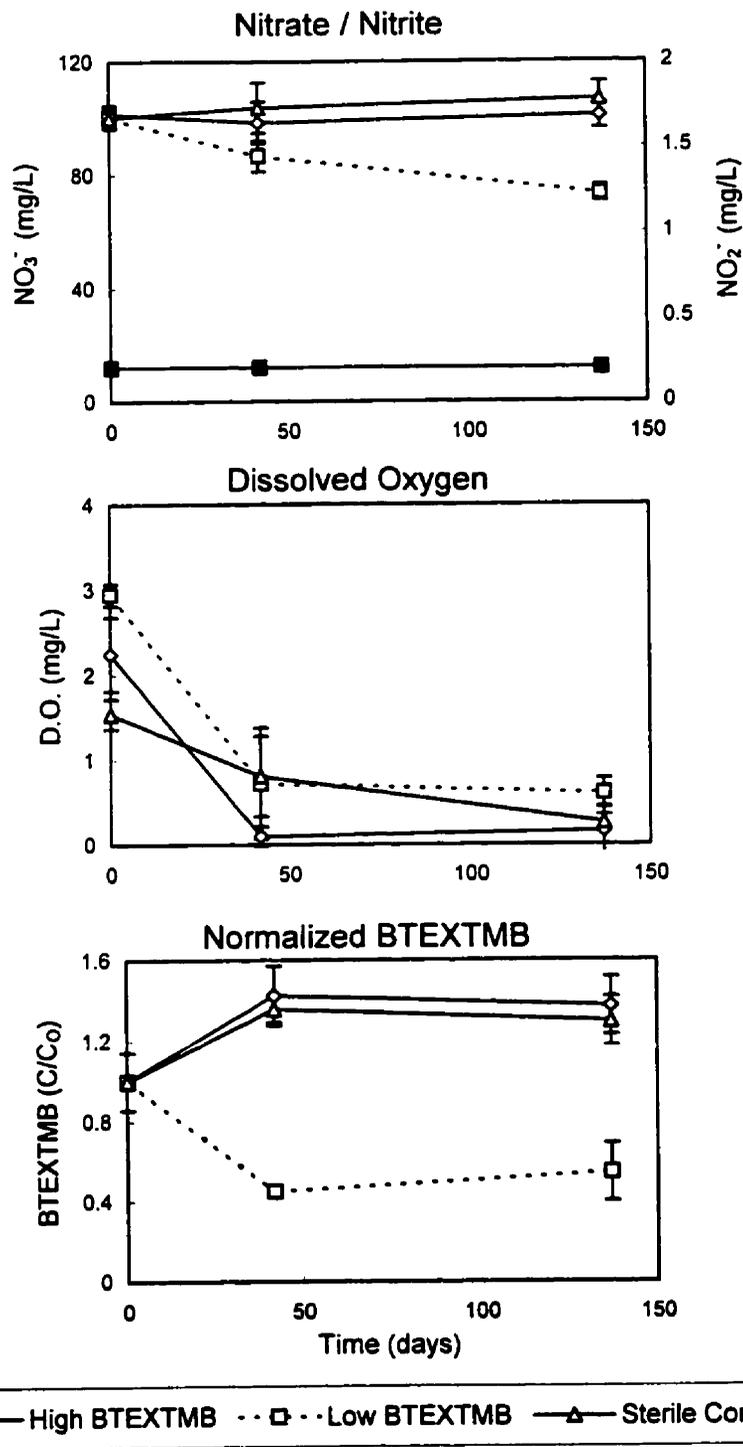


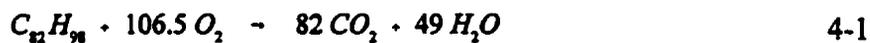
Figure 4-1. Nitrate, NO_2^- , D.O., and normalized total BTEXTMB concentrations. High BTEXTMB: gasoline-saturated; Low BTEXTMB and Control: 10x dilution. The detection limit value (0.2 mg/L) plotted for not-detected NO_2^- samples (solid squares). Plotted values are means \pm s.d. of replicate microcosms.

Table 4-3. Percent of individual aromatic hydrocarbons remaining in active, low-substrate concentration microcosms relative to sterile controls. Microcosms were amended with an air headspace and NO₃⁻, and contained pristine aquifer material.

Compound	Day 137
	% Remaining (s.d.)
Benzene	86 (14)
Toluene	10 (12)
Ethylbenzene	28 (56)
<i>m+p</i> -Xylene	24 (10)
<i>o</i> -Xylene	76 (15)
1,3,5-Trimethylbenzene	72 (38)
1,2,4-Trimethylbenzene	7 (10)
1,2,3-Trimethylbenzene	86 (52)
Naphthalene	43 (59)

Percent remaining calculated from $\frac{(C/C_o)_{Active}}{(C/C_o)_{Control}} \cdot 100$ where C_o is the concentration on day 0. Standard deviation of percent remaining calculated using Equation E-2.

Mineralization reaction stoichiometries suggest that the mass of O₂ in the low-substrate-concentration microcosms was sufficient to account for the observed mass losses. Assuming total BTEXTMB was aerobically mineralized to CO₂ and there was no assimilation of C by microbial cells, the mineralization reaction is



Based on Equation 4-1, the mass of O₂ in the headspace (0.6 mg O₂) would be sufficient to oxidize 0.2 mg BTEXTMB. The absolute mass loss in the active microcosms could not be determined reliably from day 0 concentrations. However, if losses were calculated as the difference between

the mean concentrations in active and sterile-control microcosms on day 137, the observed mass loss in the active microcosms was only 0.17 mg BTEXTMB. More generally, if the concentration in the 10x dilution of gasoline-saturated water (11 mg/L) was used to represent the initial substrate mass in the microcosms, the headspace O₂ mass was sufficient to mineralize about 30% as total BTEXTMB. The continued minor utilization of NO₃⁻ suggests that some of the losses shown in Table 4-3 may have occurred under denitrifying conditions, although it is conceivable that natural organic matter or other dissolved constituents in the gasoline-contacted water served as the carbon source under these conditions.

In the high-substrate-concentration microcosms, the mass of O₂ was quite low relative to the mass of substrate. Although small aerobic losses may have occurred, depletion relative to the day 0 sampling event were not observed because of the concentration increases between days 0 and 42. Consequently, the effect of microaerophilic O₂ was unclear, but based on the differences in oxygen and substrate masses, it can be speculated that the supplied O₂ had only a very limited effect. On the other hand, NO₃⁻ utilization results were unambiguous; in comparison to low-substrate-concentration microcosms, the lack of NO₃⁻ depletion clearly indicated that denitrifiers were not active in the high-substrate-concentration microcosms.

Despite the unexplained substrate concentration trends, the findings of this experiment were useful. In particular, concentration trends suggested that biotransformation of labile compounds such as toluene and denitrifying activity were negligible in the presence of high aqueous BTEXTMB concentrations under mixed microaerophilic / NO₃⁻ conditions. Results indicated therefore that near the source area, aqueous concentrations were high enough to be inhibitory to an unacclimatized denitrifying population in the Borden aquifer. It follows that nitrate-based bioremediation would not be effective in this aquifer near the source area. As discussed further in Chapter 5, however, NO₃⁻ utilization was observed in the field, suggesting that an acclimatized population did develop with exposure to gasoline hydrocarbons. More-extensive NO₃⁻ utilization was also observed in the laboratory using contaminated core material extracted from the Nitrate Cell (Section 4.2).

4.1.2 Microcosm Experiment 2

Because the microaerophilic O₂ in Experiment 1 microcosms appeared to be utilized rapidly, biotransformation in the presence of high aqueous concentrations of BTEXTMB may have been O₂ limited. To address this issue, an additional microcosm experiment was performed under fully-aerobic conditions.

Microcosms were again prepared with pristine Borden sand. All microcosms in this experiment were prepared with groundwater saturated with API 91-01 gasoline. Each microcosm contained a 4-ml headspace purged with pure O₂ rather than air to obtain a high initial dissolved O₂ concentration (and total O₂ mass) to drive aerobic reactions. Three treatment groups were used to evaluate biotransformation in the presence of high aqueous concentrations of BTEXTMB: aerobic / NO₃⁻; aerobic only, and aerobic sterile controls. All microcosms were incubated at room temperature in a laboratory cupboard. Five replicates from each treatment group were sampled on days 0, 42, 73, and 163. Groundwater was analyzed for BTEXTMB, dissolved O₂ (modified Winkler method), and NO₃⁻ / NO₂⁻, when applicable. The experimental design is summarized in Table 4-4.

To address questions that arose during the incubation, microcosms were drained of fluid on the final day of this experiment, and put aside for additional analysis. This work was done to determine whether biotransformation was responsible for observed aromatic-hydrocarbon losses. An aliquot of aquifer material was removed from nine microcosms for microbial enumeration, and then all of the active microcosms were reamended with 25-ml gasoline-saturated groundwater, NO₃⁻ where required, and nutrients. Control microcosms also received these amendments plus additional sodium azide solution. All microcosms were sealed with mininert™ valves for repetitive sampling. Reamended microcosms were then sampled periodically over the following 23 days for headspace BTEX. Aquifer material was enumerated for aerobic heterotrophs and benzene-toluene degraders using methods described in Section 3.3.1.

Table 4-4. Design summary, Experiment 2.

Treatment (Electron-Acceptor Regime)	Replicates	Sampling Events
Active, 4-ml pure O ₂ headspace, 70 mg/L BTEXTMB (gas. sat.), 25 mg/L NO ₃ ⁻ -N, N,P	5 active	4
Active, 4-ml pure O ₂ headspace, 70 mg/L BTEXTMB (gas. sat.), N,P	5 active	4
Sterile, 4-ml pure O ₂ headspace, 70 mg/L BTEXTMB (gas. sat.), N,P	5 sterile	4

Results. When concentrations are expressed as means of replicate microcosms, total BTEXTMB losses were observed in both active treatment groups (aerobic / NO₃⁻ and aerobic only) relative to the sterile controls (Figure 4-2). Mass losses were slightly more extensive in the mixed electron-acceptor microcosms. However, substrate concentrations in individual replicates were extremely variable, particularly in the active microcosms (Figure 4-3). Figure 4-2 also shows that NO₃⁻ utilization and NO₂⁻ production were again low in the presence of high substrate concentrations. Dissolved O₂ concentrations declined to about 8 mg/L by day 42 and remained steady for the remainder of the experiment. In general, there were no patterns of preferential utilization of individual compounds (Appendix F).

The extremely large variability in the extent of mass loss in the active microcosms was unexpected. The data suggest either patchy microbial activity and/or initial biomass, or abiotic losses (e.g., leakage) in individual replicates, or some combination of the two. The lower variability in control microcosms, as indicated by a visual inspection of the replicates (Figure 4-3), supports the former explanation. It is difficult, however, to fully explain these results without invoking either microcosm leakage or an unknown oxidation reaction. If the observed BTEXTMB mass loss resulted from aerobic oxidation, then from the stoichiometry of the mineralization reaction given in Equation 4-1 (106.5 moles O₂ per mole BTEXTMB), dissolved O₂ should have

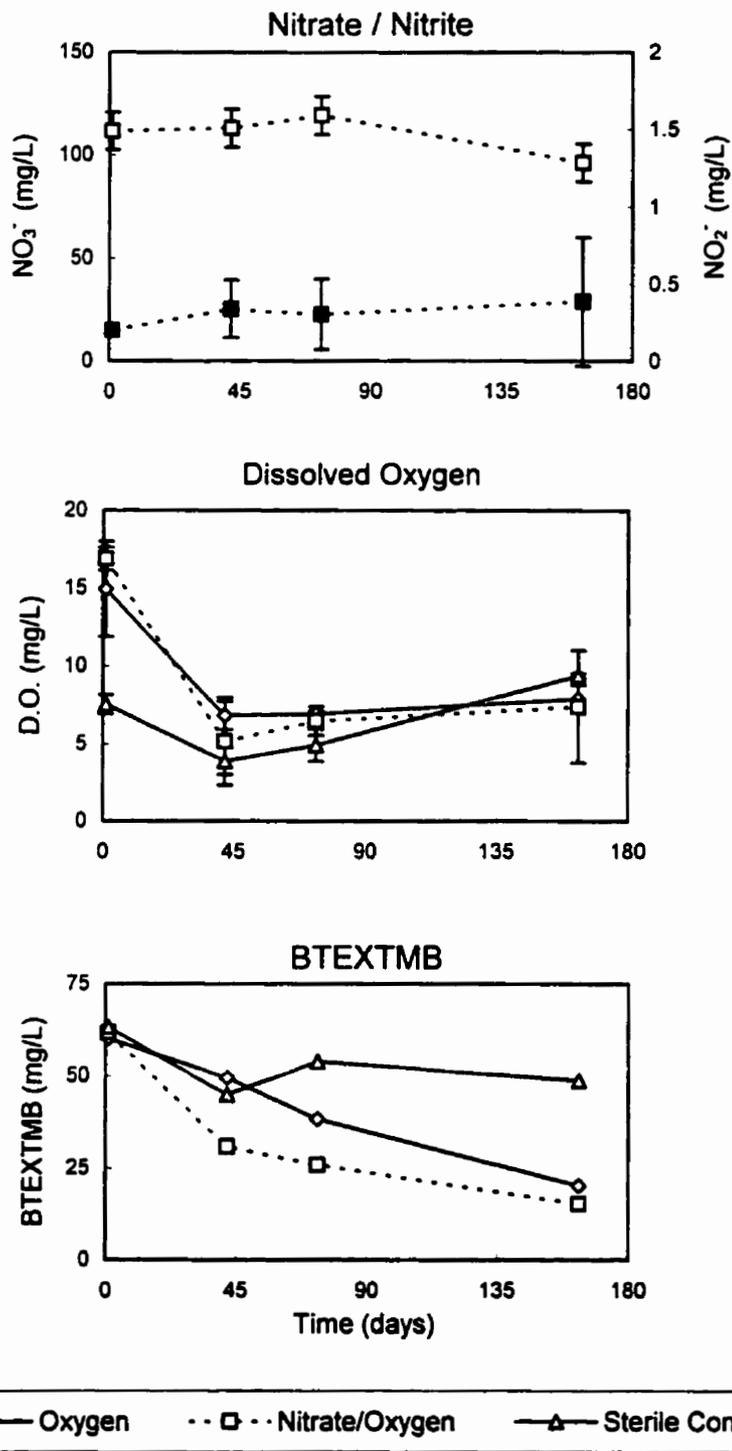


Figure 4-2. Nitrate, NO_2^- , D.O., and total BTEXTMB concentrations. The detection limit value (0.2 mg/L) plotted for not-detected NO_2^- samples (solid squares). Plotted values are means \pm s.d. of replicate microcosms. For clarity, BTEXTMB error bars not plotted.

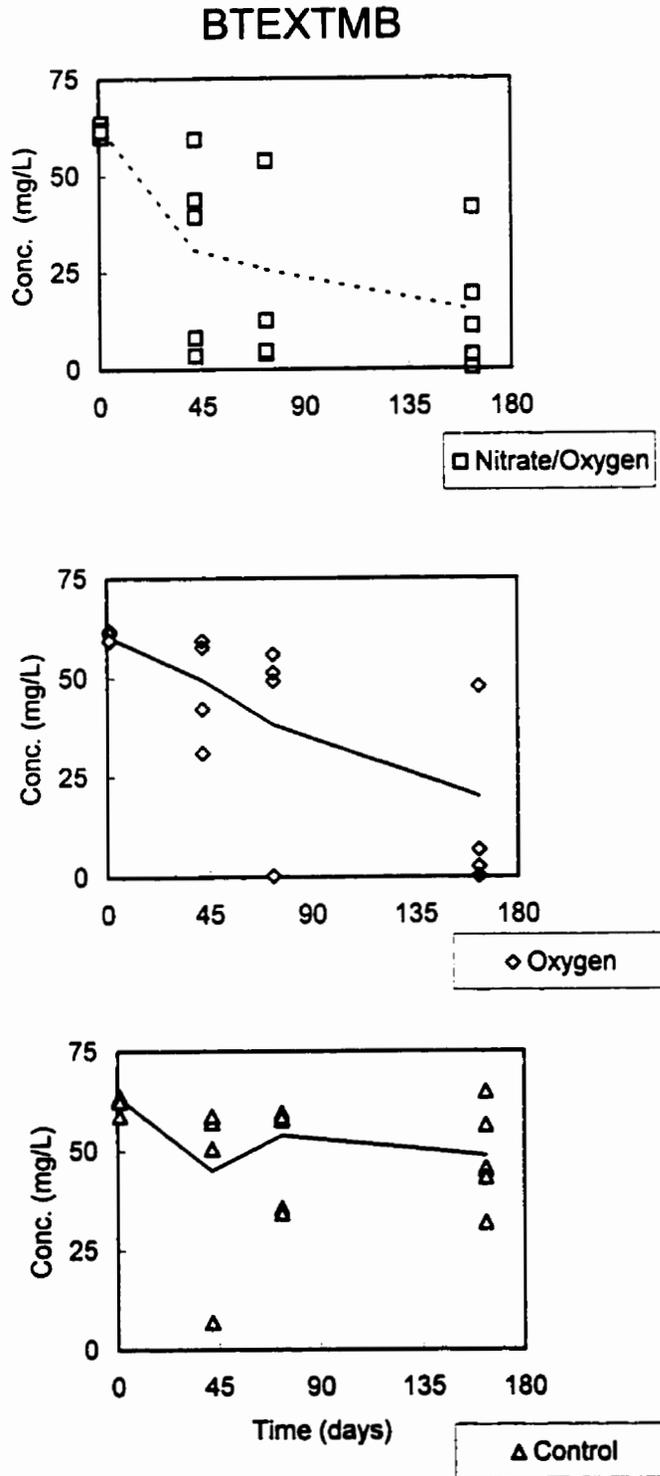


Figure 4-3. BTEXTMB concentrations in individual replicates for each of the treatment groups in Experiment 2. Lines connect mean values for each sampling event.

been completely consumed in microcosms with extensive mass loss. Complete utilization of O₂ was generally not observed (Appendix F); during this experiment depleted dissolved O₂ was observed in only two microcosms. It is conceivable that the added inorganic nutrients were insufficient to support full consumption of the O₂ mass, but corresponding substrate losses should have been low as well. In fact, if CO₂ was the major oxidation product, then from Equation 4-1 the O₂ mass supplied to the microcosms was sufficient to mineralize only 14% of the total BTEXTMB. Therefore, unless O₂ was leaking into microcosms, or mineralization was incomplete (which would not be expected with excess O₂), aerobic biotransformation cannot adequately explain these results. It is also possible that a currently undefined oxidation reaction was responsible for the mass loss. In some microcosms, an orange precipitate was observed on the surface of the aquifer sediment, but there was no clear correspondence to low BTEXTMB concentrations. The formation of a precipitate was unusual, but the reaction may have been unrelated to the observed aromatic hydrocarbon depletion (Millette et al., 1998).

Overall, the headspace BTEX results from the 23-day, post-experiment incubation suggested that microbial activity was in fact responsible for the observed substrate concentration trends. Concentrations in the individual microcosms with low aromatic-hydrocarbon concentrations on day 163 declined relative to sterile controls during the subsequent incubation period (data not shown). Similarly, concentrations in microcosms with high concentrations on day 163 did not decline relative to sterile controls. The enumeration results for the sterile-control and O₂-only microcosms also agreed quite well with the mass-loss data; low numbers were present in the microcosms with high BTEXTMB concentrations on day 163 and little mass loss during the subsequent incubation period, and vice versa. Enumeration results were more variable for the NO₃⁻ / O₂ treatment group. Enumeration data are summarized in Table 4-5. These results may be evidence that the experimental conditions (i.e., concentrations of parent compounds or metabolites) were toxic to the microbial community in some replicates, but not in others.

The rapid utilization after reamendment suggested that there was potential for aerobic biotransformation of high substrate concentrations in pristine Borden aquifer material. Because of conflicting dissolved-O₂ data and the large variability in aromatic-hydrocarbon concentrations, however, the possibility of experimental artifact cannot be eliminated. If microbial activity was responsible for the observed mass losses, the distribution of populations tolerant of high

Table 4-5. Microbial enumerations and hydrocarbon degrading activity for nine replicates selected for reamendment after day 163.

Replicate	Day 163 Total BTEXTMB Concentration (mg/L)	Heterotrophic Plate Count (CFU/g wet wt.) (s.d.)	Benzene-Toluene Degraders (MPN/g wet wt.)	Hydrocarbon-Degrading Activity After Reamendment
Control A	65.0	n.d.	n.d.	(-)
Control B	32.0	5.7×10^2 (3.7×10^2)	n.d.	(-)
Control E	56.4	n.d.	n.d.	(-)
O ₂ A	0.0	9.0×10^7 (1.0×10^7)	2.0×10^3	(+)
O ₂ C	47.9	4.0×10^5 (4.8×10^4)	23	(-)
O ₂ E	2.6	2.7×10^6 (7.3×10^4)	4.3×10^2	(+)
O ₂ /NO ₃ ⁻ A	41.6	1.3×10^6 (9.5×10^4)	2.1×10^2	(+)
O ₂ /NO ₃ ⁻ C	19.3	1.5×10^6 (1.6×10^5)	1.5×10^3	(+)
O ₂ /NO ₃ ⁻ E	3.6	4.3×10^7 (2.6×10^6)	43	(+)

n.d. - none detected. Determination of hydrocarbon degrading activity after reamendment based on observed compound losses.

concentrations would appear to be patchy in pristine aquifer material. This is consistent with the results of Butler et al. (1997) who found that microbial populations were very localized in the Borden aquifer. Distinct populations with varying metabolic capabilities were observed within a 5.5 m^2 area. In contrast, the large and consistent O_2 demand among replicates containing gasoline-contaminated aquifer material extracted from the Nitrate Cell (Section 4.2) indicated that some adaptation to the presence of gasoline had occurred within and below the gasoline source area.

4.2 Microcosm Experiments: Gasoline-Contaminated Borden Sand

4.2.1 Microcosm Experiment 3

This main purpose of this follow-up experiment was to collect additional experimental data on electron-acceptor and aromatic-hydrocarbon utilization under conditions similar to those established in the Nitrate Cell. The effect of *in situ* gasoline exposure was also investigated by comparing trends in electron-acceptor and substrate utilization with pristine aquifer material (Experiments 1 and 2). When cores were collected in July, 1997 from the Nitrate Cell, the aquifer material had been exposed to gasoline (aqueous or pure-phase) for 19 months, and to NO_3^- for 14 months.

Microcosms were prepared with core material extracted from the Nitrate Cell. Core from a depth interval of approximately 80 to 180 cm bgs was used in the experiment. Before dispensing to microcosms, most of the residual gasoline phase was removed by saturating the aquifer material with sterile water, gently stirring the resulting slurry, and then draining the liquid phase. This was done to remove as much of the existing aqueous aromatics and residual gasoline as possible, with minimal disturbance to the microbial population. Analysis of the washed material indicated that this procedure was successful in lowering aqueous concentrations of benzene, toluene, and ethylbenzene, but mg/L concentrations of the less-soluble aromatics remained (Appendix F). This indicates that the washing procedure did not completely remove the residual gasoline phase, which contained substantial concentrations of these constituents at the end of the field experiment. With the exception of one low-substrate-concentration treatment group, all microcosms were set up with gasoline-saturated groundwater to approximate field conditions. Because a residual phase was still

present, initial concentrations of the xylene isomers, trimethylbenzene isomers, and naphthalene were near gasoline-saturated concentrations in the low-concentration (10x dilution) microcosms; as a result the measured day 1 total BTEXTMB concentration was 19.5 mg/L (see Figure 4-5c).

Five treatment groups were used to isolate the effects of electron-acceptor regime and substrate concentration in contaminated aquifer material: microaerophilic / NO_3^- ; aerobic / NO_3^- ; microaerophilic / NO_3^- plus low-BTEXTMB (10x dilution of gasoline-saturated water), unamended (no O_2 / NO_3^-), and a microaerophilic / NO_3^- sterile control. All microcosms except the low-BTEXTMB group were prepared with gasoline-saturated water and O_2 was added to headspaces as described previously. The microaerophilic (low O_2) microcosms were incubated in the anaerobic chamber. The aerobic (high- O_2) microcosms were incubated initially in a laboratory cupboard, but were moved to the anaerobic chamber on day 82 of the experiment. It should be noted that, in general, treatment groups should not be segregated because differences between locations can potentially lead to spurious treatment effects (Hurlbert, 1984); fortunately in this instance the effect of fully-aerobic conditions was obvious, during incubation both within and outside of the anaerobic chamber. Groundwater was analyzed for BTEXTMB, dissolved O_2 (with the O_2 meter), NO_3^- , and NO_2^- . Extra replicates of each treatment group were also prepared for a denitrification assay (acetylene block). These microcosms were analyzed for N_2O in addition to the other parameters. The design is summarized in Table 4-6.

In response to rapid dissolved O_2 and NO_3^- utilization in the microcosms amended with pure O_2 , several modifications were made to the experimental design. On day 82, NO_3^- was respiked into these microcosms to determine if rapid NO_3^- utilization would continue under anaerobic conditions. Microcosms were amended and subsequently incubated inside the anaerobic chamber to maintain anoxic conditions. At the same time, duplicate microcosms from all treatments except the unamended group were spiked with acetylene and sampled after 15 days of incubation in the anaerobic chamber. Finally, on day 154, the headspaces of all remaining microcosms except the unamended group were flushed with pure O_2 to determine if biotransformation of aromatic hydrocarbons would be stimulated under aerobic conditions. To accommodate these changes, microcosms were sacrificed and sampled more frequently over a 173 day incubation period. Microcosms were sampled in triplicate for the first three sampling events, and in duplicate or singly thereafter.

Table 4-6. Design summary, Experiment 3.

Treatment (Electron Acceptor Regime, BTEXTMB Concentration)	Replicates	Expected Sampling Events
Active, 100 mg/L BTEXTMB (gas. sat.), 2-ml air headspace, 25 mg/L NO ₃ ⁻ -N, N,P	3	4
Active, 100 mg/L BTEXTMB (gas. sat.), 4-ml pure O ₂ headspace, 25 mg/L NO ₃ ⁻ -N, N,P	3	4
Active, 10 mg/L BTEXTMB (10x dil.), 2-ml air headspace, 25 mg/L NO ₃ ⁻ -N, N,P	3	4
Active, 100 mg/L BTEXTMB (gas. sat.), N,P	3	4
Sterile, 100 mg/L BTEXTMB (gas. sat.), 2-ml air headspace, 25 mg/L NO ₃ ⁻ -N, N,P	3 sterile	4
Aqueous Sterile (no aquifer material), 90 mg/L BTEXTMB (neat), 4-ml pure O ₂ headspace	3 sterile	4
Aqueous Sterile (no aquifer material), 90 mg/L BTEXTMB (neat), 2-ml air headspace	3 sterile	4

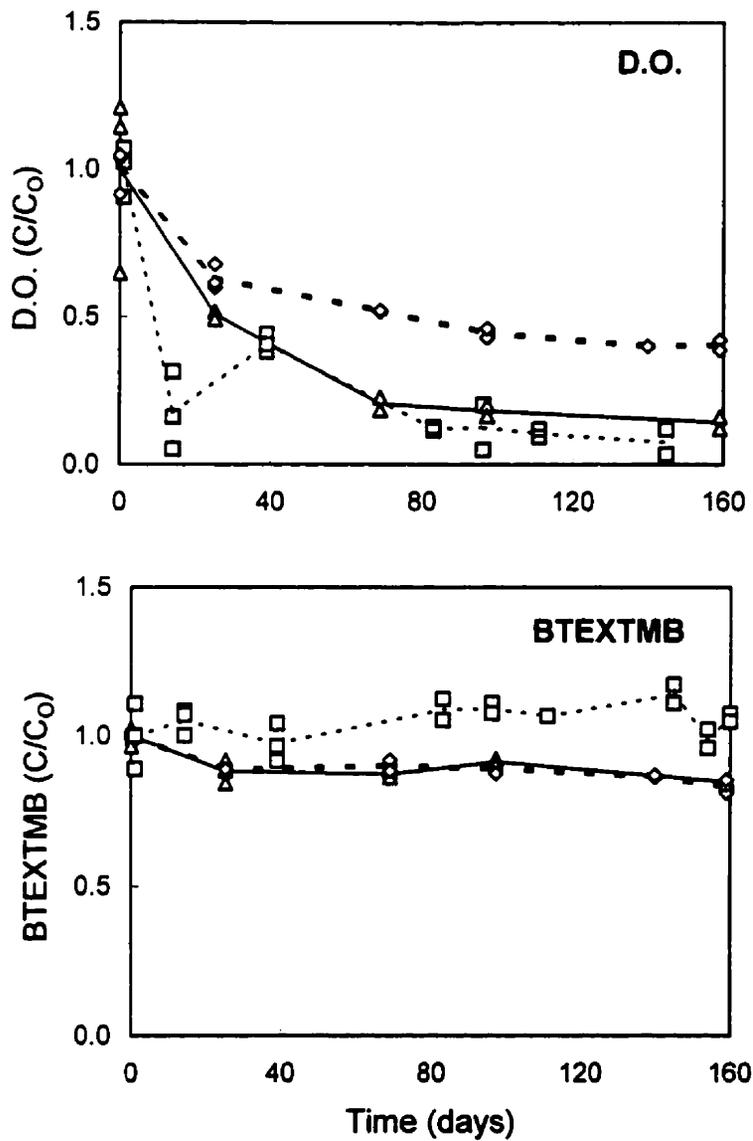
Aqueous (no aquifer material) sterile-control microcosms designed to investigate abiotic losses of dissolved O₂ and aromatic hydrocarbons were also prepared and incubated with other Experiment 3 microcosms (Table 4-6). Microcosms were sampled and analyzed for aromatic hydrocarbons and dissolved O₂ (using the O₂ meter) periodically between days 0 and 159.

Results. The aromatic hydrocarbons in the unamended microcosms did not decline relative to the sterile controls; other microbial populations (e.g., Fe or SO₄²⁻ reducers) were therefore not degrading aromatic-hydrocarbons at a detectable rate. For brevity, unamended microcosm results are not shown or discussed further.

The aqueous-sterile-control microcosms were sampled on day 0, several hours after preparation; measured concentrations showed that the 2-ml air and 4-ml pure O₂ headspaces provided 4.9 mg/L and 26.2 mg/L initial dissolved O₂, respectively. Losses of dissolved O₂ occurred during storage both inside (microaerophilic controls) and outside (aerobic controls) the anaerobic chamber, as microcosms equilibrated with the external atmosphere over a four-month period (Figure 4-4). The rate of loss was, however, much lower than in active microcosms. Rapid leakage around seals did not occur. The good agreement between the microaerophilic controls with and without aquifer material indicated that the abiotic O₂ demand of the contaminated aquifer material was quite low. This may indicate that the redox potential in the Nitrate Cell was buffered by the continuous presence of NO₃⁻; and consequently, that significant quantities of reduced inorganic species such as Fe and Mn that are capable of reacting abiotically with O₂ were not produced. In contrast to O₂, diffusive losses of aqueous BTEXTMB in both aqueous and conventional (i.e., containing aquifer material) sterile controls were low over the incubation period (Figure 4-4).

Aromatic-hydrocarbon losses relative to sterile controls were observed in all active gasoline-saturated microcosms during the 24-hour period between preparation and the first sampling event (Figures 4-5a and 4-5b). The extent of consumption corresponded to the mass of O₂ in the microcosm. For example, the largest decline during early time occurred in the microcosms amended with pure O₂ (Figure 4-5a). In contrast, in the high-substrate-concentration microcosms amended with microaerophilic O₂ and NO₃⁻, the conditions most analogous to the Nitrate Cell, substrate concentrations were very similar to sterile-controls (Figure 4-5b); microaerophilic O₂ therefore had only a minor effect on mass loss. This result is consistent with field observations.

Continued aromatic-hydrocarbon losses under anaerobic conditions were minor. Normalized mean concentrations of selected individual aromatic hydrocarbons are shown in Figures 4-6 through 4-8 for the microaerophilic and sterile-control treatment groups. Percentage losses of individual compounds for the two microaerophilic / NO₃⁻ treatment groups (high- and low-BTEXTMB concentration) are also shown on Table 4-7. It should be noted that because the microaerophilic O₂ was essentially consumed by day 1, and losses were calculated relative to day 1 concentrations, depletion of aromatics between days 1 and 145 occurred primarily under

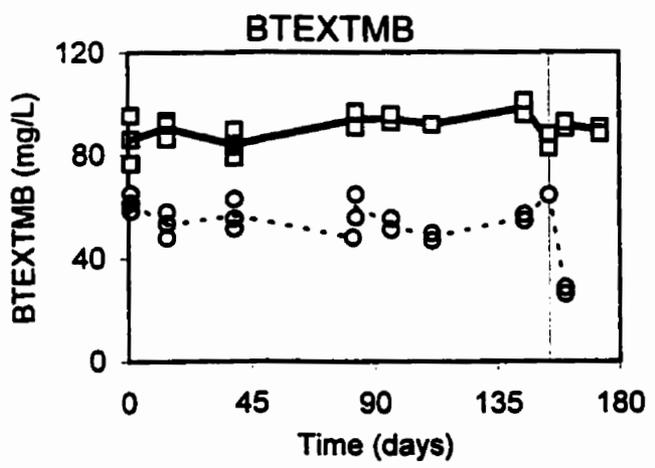
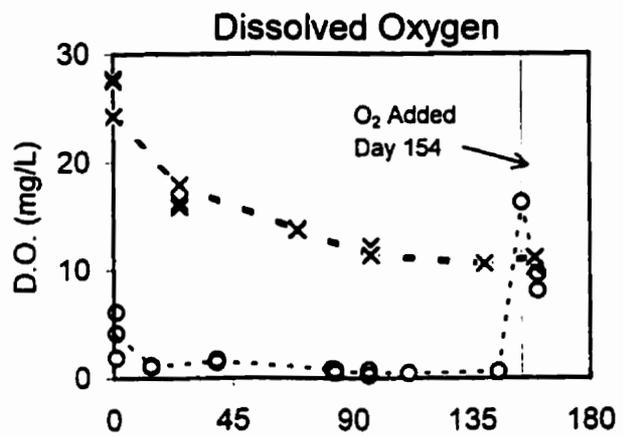
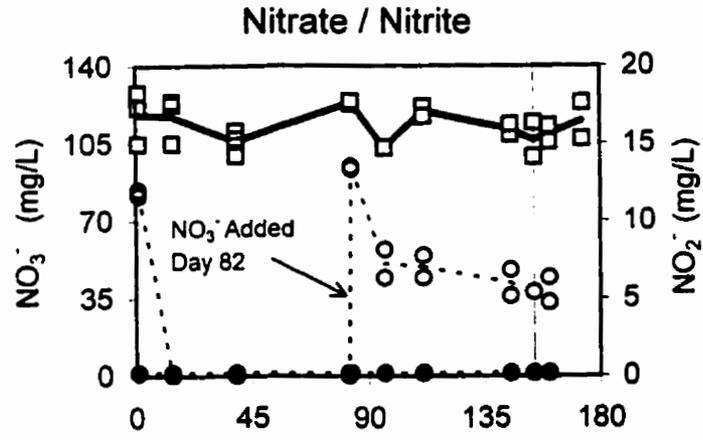


▲ Microaerophilic Aqueous ◇ Aerobic Aqueous
 □ Microaerophilic Aqueous/Sediment

Figure 4-4. Normalized D.O. and total BTEXTMB concentrations in sterile microcosms with and without gasoline-contaminated aquifer material. Lines connect single values or means of duplicate and triplicate replicates.

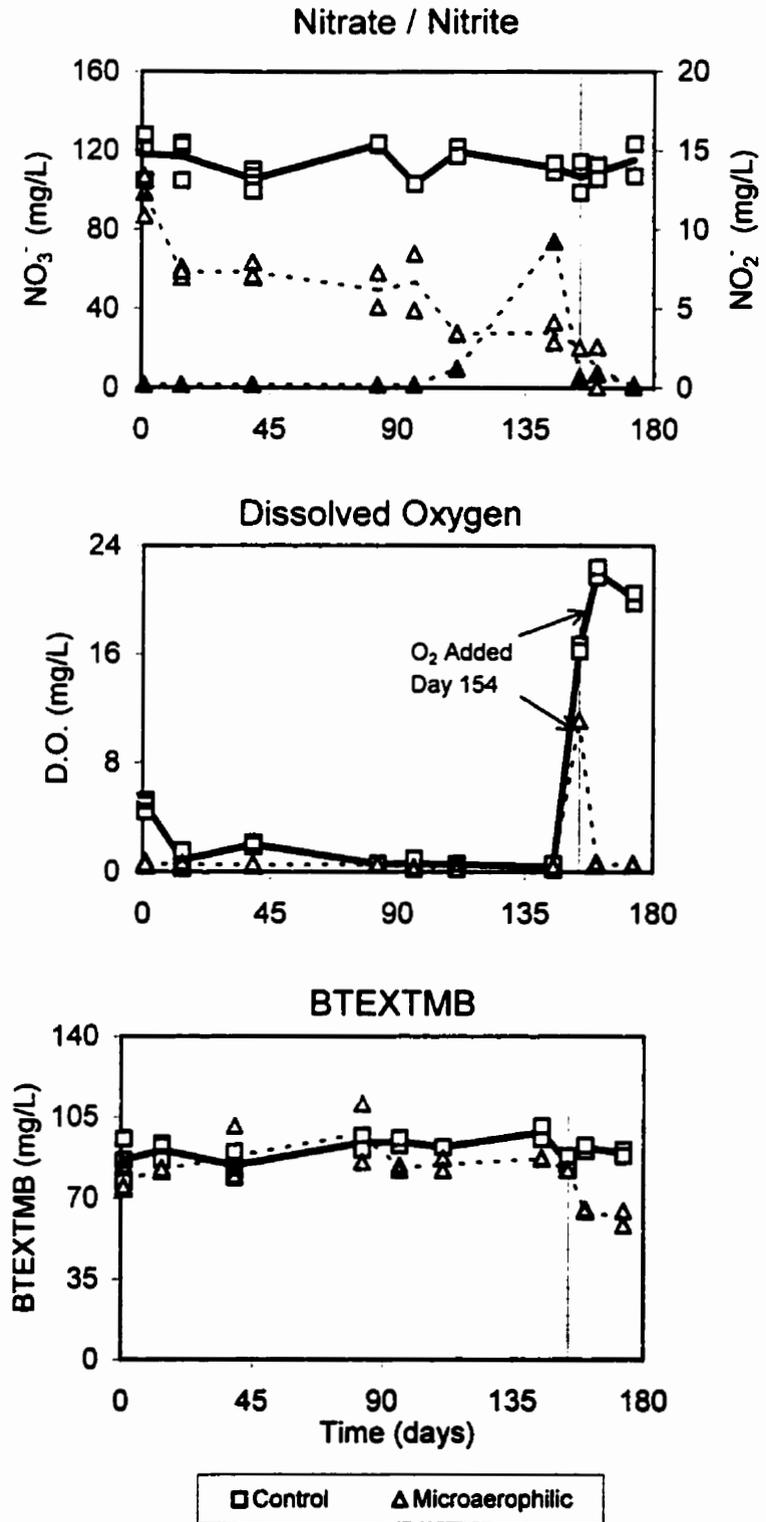
Figure 4-5. (Following Pages) Nitrate, NO_2^- , D.O. and total BTEXTMB concentrations in active and sterile-control microcosms with gasoline-contaminated aquifer material from the Nitrate Cell. (a) Aerobic (high O_2) treatment. (b) Microaerophilic (low O_2) treatment. (c) Microaerophilic, 10x dilution treatment. Oxygen added to all microcosms on day 154 except high- O_2 aqueous control plotted on (a). Nitrite not detected in sterile controls; for clarity, data not shown on plots. Nitrite in active microcosms plotted as solid symbols. Lines connect single values or means of duplicate and triplicate replicates.

(a)

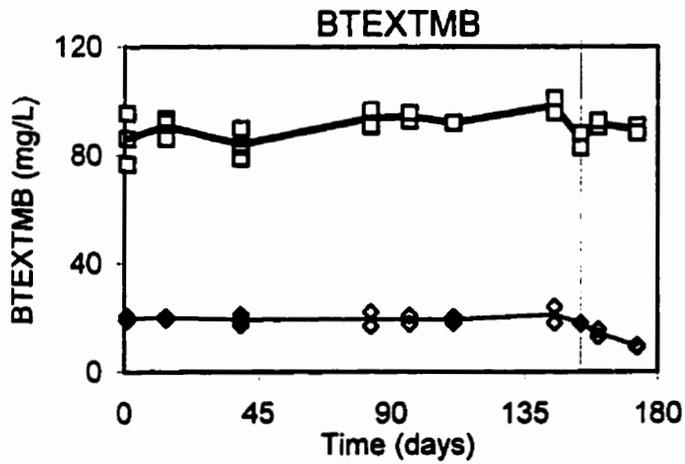
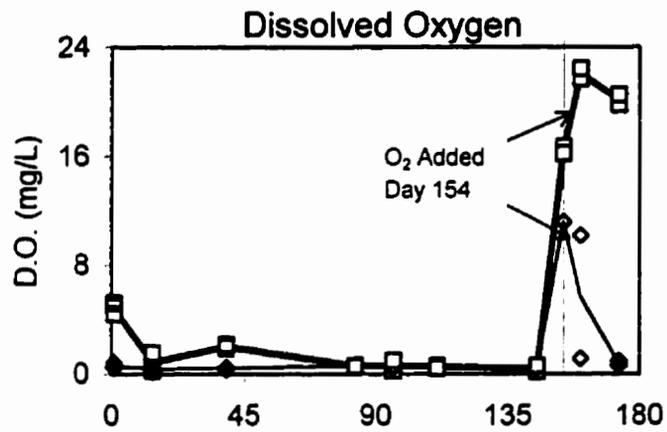
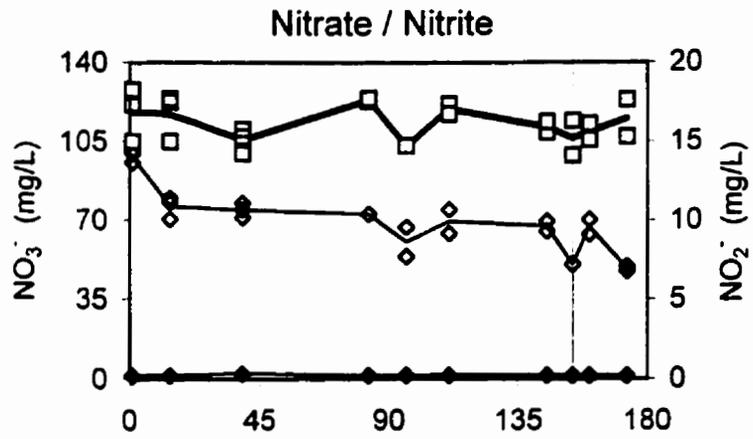


□ Control ○ Aerobic X Aerobic Aqueous Control

(b)

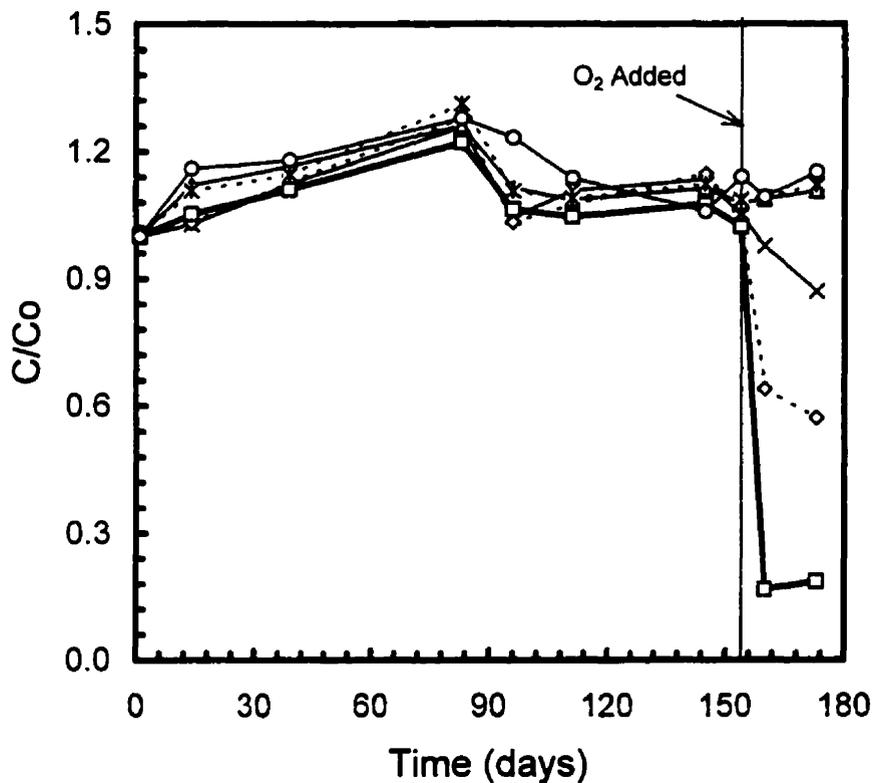


(C)



□ Control ♦ Microaerophilic, 10x dil.

Microaerophilic / NO₃
Gasoline-Saturated



—x— Ben ..◇.. Tol —□— Eben —△— m+p-Xyl ..*..o-Xyl —○— 1,2,4-TMB

Figure 4-6. Normalized concentrations of selected aromatic hydrocarbons in gasoline-contaminated aquifer material amended with microaerophilic O₂, NO₃⁻, and gasoline-saturated water. Lines join means of replicate microcosms. For clarity, replicates not plotted; variability as total BTEXTMB shown on Figure 4-5b.

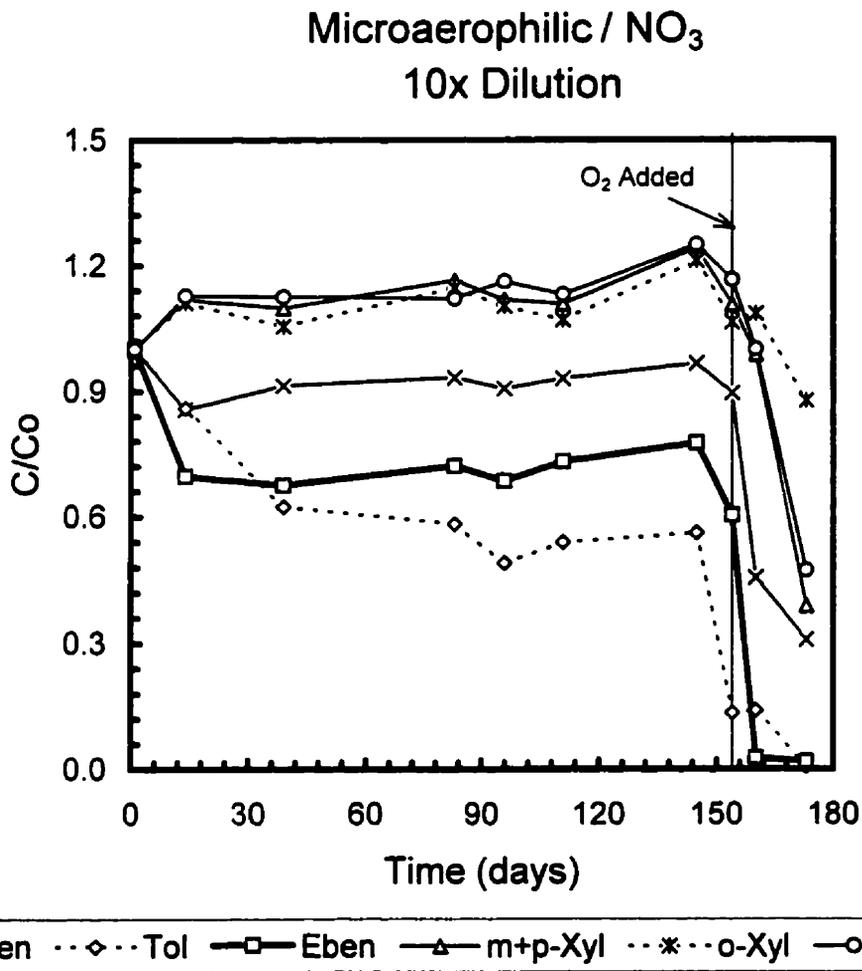
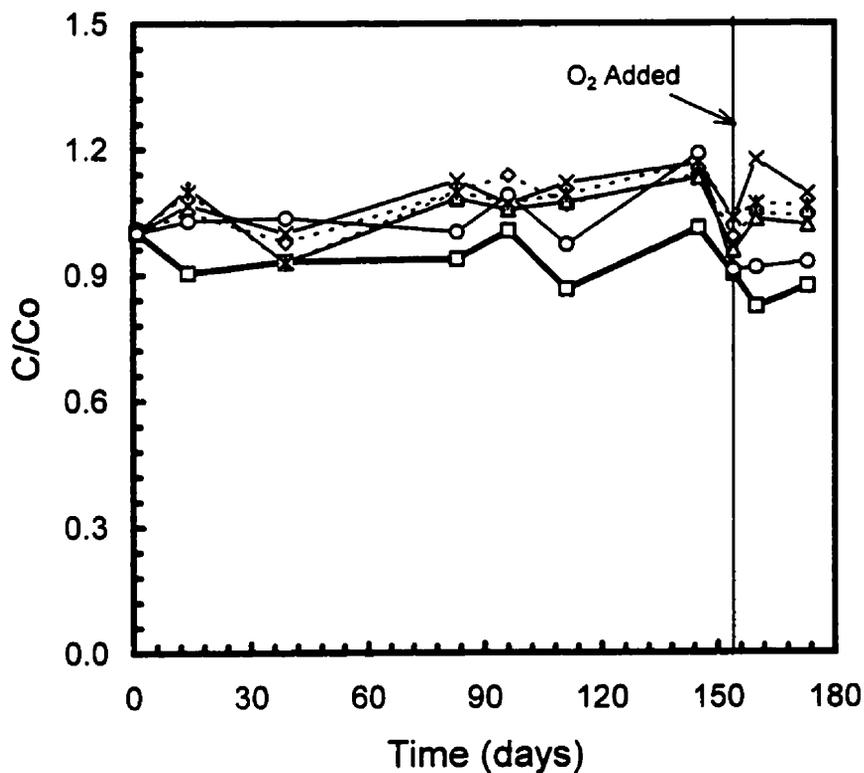


Figure 4-7. Normalized concentrations of selected aromatic hydrocarbons in gasoline-contaminated aquifer material amended with microaerophilic O₂, NO₃⁻, and 10x dilution of gasoline-saturated water. Lines join means of replicate microcosms. For clarity, replicates not plotted; variability as total BTEXTMB shown on Figure 4-5c.

**Sterile, Microaerophilic / NO₃
Gasoline-Saturated**



—x— Ben ··◇·· Tol —□— Eben —△— m+p-Xyl ··*··o-Xyl —○— 1,2,4-TMB

Figure 4-8. Normalized concentrations of selected aromatic hydrocarbons in sterile gasoline-contaminated aquifer material amended with microaerophilic O₂, NO₃, and gasoline-saturated water. Lines join means of replicate microcosms. For clarity, replicates not plotted; variability as total BTEXTMB shown on Figure 4-5.

anaerobic conditions, probably at the expense of NO_3^- . In the low-substrate-concentration microcosms, both toluene and ethylbenzene declined under anaerobic conditions, but toluene concentrations were quite variable among replicate microcosms (Appendix F). When O_2 was added on day 154, substantial losses of benzene, toluene, ethylbenzene, *m+p*-xylenes, and 1,2,4-trimethylbenzene were observed in these microcosms. The apparent declines in aromatic-hydrocarbon concentrations prior to the day-154 O_2 addition were likely caused by rapid aerobic biotransformation during the several hours that elapsed between the O_2 spike and microcosm sampling (Figure 4-7).

In contrast, in the high-substrate-concentration microcosms there were negligible losses under anaerobic conditions, and only benzene, toluene, and ethylbenzene concentrations declined after O_2 reamendment. 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, and naphthalene appeared recalcitrant under these incubation conditions. It is unclear why the observed trimethylbenzene isomers and naphthalene ratios are higher on day 173 relative to day 145. One plausible explanation is that concentrations declined more in the sterile controls than in the active treatments when the microcosms were opened on day 154 to replenish headspaces with O_2 . This probably resulted from removal or extensive depletion of the residual gasoline during preparation (i.e., autoclaving) of the aquifer material for the sterile controls. Consequently, it is possible that although the relatively-insoluble aromatics appeared recalcitrant in active microcosms, the residual gasoline acted as a reservoir and obscured minor biotransformation in the aqueous phase.

In the microcosms amended with pure O_2 , the initial dissolved O_2 concentration (26 mg/L, assumed from aqueous sterile controls) declined rapidly (Figure 4-5a). In both of the microaerophilic treatment groups, the dissolved O_2 concentration also dropped rapidly, from an initial concentration of 5 mg/L (assumed from sterile control microcosms) to an apparent threshold concentration within 24 hours. When microcosms were reamended with pure O_2 on day 154, rapid substrate and dissolved O_2 depletion were again observed in all active microcosms (Figures 4-5a-c, 4-6, 4-7, and 4-8). These responses demonstrated that an acclimated aerobic population was present in the contaminated aquifer material, and that dissolved O_2 was required for biotransformation of the aromatic hydrocarbons (with the possible exceptions of toluene and ethylbenzene when present at a 10x dilution of gasoline-saturated levels).

Table 4-7. Percent of individual aromatic hydrocarbons remaining in active low- and high-substrate concentration microcosms relative to sterile controls. Microcosms were amended initially with an air headspace and NO₃⁻, and contained gasoline-contaminated aquifer material from the Nitrate Cell.

Compound	% Remaining Relative to Sterile Controls			
	10x Dilution of Gasoline-Saturated Water (2-ml Air Headspace)		Gasoline-Saturated Water (2-ml Air Headspace)	
	Day 145 (O ₂ depleted)	Day 173 (19 days after pure-O ₂ addition)	Day 145 (O ₂ depleted)	Day 173 (19 days after pure-O ₂ addition)
Benzene	83.	28.	97.	80.
Toluene	50.	0.7	101.	55.
Ethylbenzene	77.	2.	106.	21.
<i>m+p</i> -xylene	101.	38.	98.	109.
<i>o</i> -xylene	104.	83.	96.	105.
1,3,5-Trimethylbenzene	106.	130.	90.	127.
1,2,4-Trimethylbenzene	105.	51.	89.	124.
1,2,3-Trimethylbenzene	104.	122.	87.	120.
Naphthalene	98.	110.	84.	125.

Percent remaining for a given sampling event calculated from $\frac{(C/C_0)_{Active}}{(C/C_0)_{Control}} \cdot 100$, where all concentrations are means of replicate microcosms, and C₀ = day 1 of incubation.

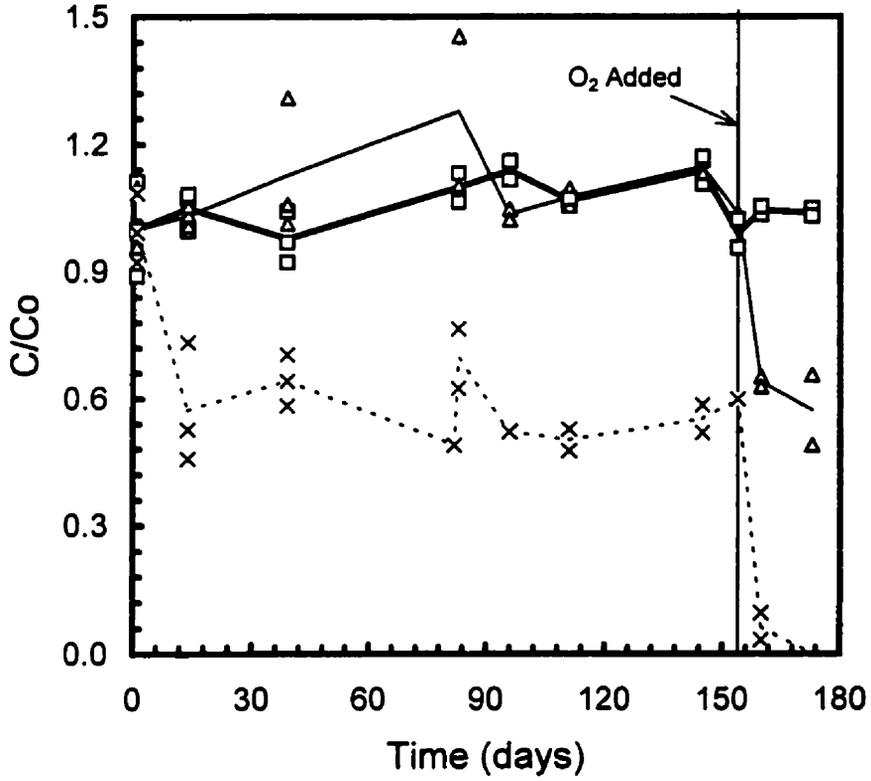
The utilization of NO_3^- varied depending on the treatment group. The one similarity was that NO_3^- was depleted in all three active treatments relative to the sterile controls during the first 24 hours of the experiment when O_2 was present. The most extensive utilization occurred in the aerobic microcosms, where NO_3^- was completely consumed by day 14 (Figure 4-5a). The rapid consumption of NO_3^- in these microcosms was surprising because such rapid losses had not been observed in the Nitrate Cell. One possible explanation is that the NO_3^- was being utilized as an assimilatory nitrogen source during aerobic biotransformation; because the mass of O_2 and available hydrocarbons in these microcosms was large, the mass of $\text{NH}_4\text{-N}$ may have been insufficient to meet the assimilatory N demand. When NO_3^- was replenished on day 82, additional NO_3^- utilization was observed under anaerobic conditions, but the rate was considerably lower (Figure 4-5a). The production of N_2O in acetylene-amended microcosms between days 82 and 97 suggested that denitrification was occurring in these microcosms (Table 4-8).

Utilization of NO_3^- in the microaerophilic, high-substrate-concentration microcosms was considerably slower than in the pure O_2 treatment (Figure 4-5b). A comparison of these results with those of Experiment 1 clearly indicates, however, that anaerobic NO_3^- utilization in the presence of high aqueous concentrations of the aromatic hydrocarbons increased after prolonged exposure to hydrocarbon contamination. These NO_3^- data yielded a zero-order (linear) depletion rate of 0.43 mg/L/d, which is within the range of rates measured in the Nitrate Cell (see Section 5.1.2). Although NO_3^- declined, utilization of the substrates that are typically labile under denitrifying conditions (toluene or ethylbenzene) was not evident. Toluene mass losses in the high-substrate-concentration treatment groups are shown in Figure 4-9; it is clear from this figure that anaerobic toluene losses in the microaerophilic treatment were negligible.

Table 4-8. Dissolved nitrous oxide concentrations in selected microcosms containing contaminated aquifer material from the Nitrate Cell. Nitrate was present in all microcosms when analyzed. Acetylene was added on day 82, 15 days prior to analysis.

Individual Microcosm	Acetylene Added	Dissolved N ₂ O (mg/L)
Aerobic, gas.-sat.	(+)	5.45
Aerobic, gas.-sat.	(+)	9.64
Aerobic, gas.-sat.	(-)	<0.45
Microaerophilic, gas.-sat.	(+)	<0.45
Microaerophilic, gas.-sat.	(+)	<0.45
Microaerophilic, gas.-sat.	(-)	<0.45
Microaerophilic, 10x dil.	(+)	0.39
Microaerophilic, 10x dil.	(+)	1.00
Microaerophilic, 10x dil.	(-)	<0.45
Sterile Control	(+)	<0.45
Sterile Control	(+)	<0.45

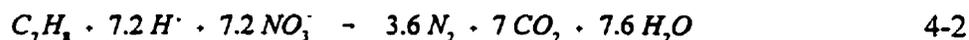
Toluene Mass Loss



— Sterile — Microaerophilic ····· Aerobic

Figure 4-9. Normalized toluene concentrations in gasoline-contaminated aquifer material amended with gasoline-saturated water. Lines connect single values or means of duplicate and triplicate replicates.

Assuming toluene was mineralized in a denitrification reaction, and there was no assimilation of C and N by microbial cells, mass loss is governed by



Consequently, using an initial toluene concentration of 40 mg/L (2 mg initial mass), consumption of 25 mg/L NO_3^- -N (5 mg NO_3^- initial mass) would have produced an observable decrease in toluene mass of about 50% by the end of the experiment. However, the denitrification assay was negative in duplicate microcosms spiked with acetylene (Table 4-8). Therefore, the possibility that NO_3^- was used primarily to satisfy an N demand for an undefined, anaerobic reaction cannot be eliminated. On the other hand NO_2^- accumulation was observed in these microcosms on day 82 and consistently in the Nitrate Cell. If denitrifying activity was responsible for observed NO_3^- utilization, the labile aromatic hydrocarbons were either recalcitrant or utilized at a very low rate. This may reflect preferential utilization of other aqueous constituents in the gasoline-saturated water, or insoluble constituents in the gasoline phase.

In contrast, in the microaerophilic, low-substrate-concentration microcosms there was less NO_3^- utilization, and no observable NO_2^- accumulation (Figure 4-5c), but there were minor losses of toluene and ethylbenzene under anaerobic conditions (Table 4-9), and the denitrification assay was positive (Table 4-8). The reasons for the differences in the occurrence of denitrification and extent of NO_3^- utilization in these two microaerophilic treatments were not evident from the data collected in this experiment.

4.3 Microbial Characterization Results

Microbial enumerations and activity measurements were used as additional indirect lines of evidence for *in situ* biotransformation of gasoline hydrocarbons. Patterns of microbial activity and numbers, in conjunction with other lines of evidence, have been used in other studies to document biotransformation in contaminated aquifers (Harvey et al., 1984; Song and Bartha, 1990; Madsen et al., 1991; Williams et al., 1997). In this study, numbers and activity in pristine Borden aquifer material were compared with material extracted from the treatment cells (19 month exposure to aqueous- or pure-phase gasoline). A detailed characterization of the microbial populations of the Borden aquifer, including changes that occurred in response to hydrocarbon contamination, is provided by Butler et al. (1997).

4.3.1 Pristine Aquifer Material

Enumerations. Several cores collected near the field site for use in laboratory experiments were enumerated to determine the numbers of aerobic heterotrophs and denitrifiers in background (pristine) Borden aquifer material (Table 4-9). In all cases, core material from the shallow saturated zone (depths less than two meters below the water table) was used. The majority of the cores were collected in 1993 or 1994, near the beginning of the study, and enumerated when used for an experiment. Core 2-2 was collected in June, 1997, and enumerated in September, 1997. All cores were collected in the northeast corner of the sand pit, within about 100 m of the treatment cells. Results indicate that the age of the core had no consistent effect on the numbers of culturable organisms or the ability to biotransform TEX under denitrifying conditions (Table 4-9).

Counts of viable, aerobic heterotrophs in pristine aquifer material varied by about two orders of magnitude (Table 4-9). HPCs ranged from 6×10^4 CFU/g (colony forming units per gram) to 1×10^6 CFU/g. Counts from these cores were consistent with other studies of pristine Borden aquifer material (Barbaro et al., 1994; Butler et al., 1997). Using a much larger set of data, Barbaro et al. (1994) found that the numbers of aerobic, culturable microorganisms in the upper 2 m of the aquifer varied by more than six orders of magnitude, and were correlated strongly with depth and *in situ* dissolved-O₂ concentration. Denitrifier numbers were more variable than aerobic heterotrophs in the cores collected in the current study, with a range from 3×10^2 MPN/g

(most probable number per gram) to 1×10^6 MPN/g (Table 4-9). As noted by Butler et al. (1997), the magnitudes of the aerobic heterotroph and denitrifier counts are similar enough to suggest that a substantial fraction of the population in pristine material has the capacity to denitrify. Overall, the numbers of culturable microorganisms in Borden aquifer material were consistent with numbers obtained in other shallow, sandy aquifers (e.g., Beloin et al., 1988).

Table 4-9. Microbial enumerations of Borden cores.

Core I.D.	Heterotrophic Plate Counts (CFU/g dry wt)	Denitrifiers (MPN/g dry wt)	Approx. Core Age (months) ¹	TEX ³ Degradation with NO ₃ ⁻
#7-93	6.2×10^4	1.7×10^4	6	(+)
#5-93	1.1×10^5	2.8×10^2	8	(+) (1 of 3 replicates)
#4-93	1.2×10^5	2.5×10^3	11	(-)
#2-94	1.25×10^6	2.7×10^5	1	(+)
#6-93	n.t.	n.t.	8	(-) ²
#2-93	5.8×10^5	1.2×10^6	13	(+)
#1-94/#3-94 composite	1.1×10^6	4.9×10^4	2	(+)
#2-2	6.1×10^5	4.3×10^3	3	n.t.

¹ months of storage at 4°C before use. ² a few replicates (+) after ca. 1 year incubation.

³ Degradation data provided in Barbaro et al. (1998). n.t. not tested.

4.3.2. Gasoline-Contaminated Aquifer Material

Enumerations. To compare pristine and gasoline-contaminated aquifer material, aquifer material from cores extracted aseptically from the treatment cells (July, 1997) was also enumerated for selected populations that might have responded to conditions established in the field: aerobic heterotrophs, denitrifiers, and aerobic benzene-toluene degraders. Two aquifer samples were enumerated from each cell: A shallow sample from the 50 to 80 cm bgs interval that contained a residual gasoline phase, and a deep sample from 155 to 190 cm bgs interval that had been exposed to high aqueous concentrations but not to gasoline. The results are summarized on Figure 4-10. For comparison with pristine material, the sample from Core 2-2, which was prepared and incubated with the contaminated samples, is also plotted on this figure. Viable, aerobic heterotrophs ranged from 5×10^4 CFU/g (shallow Control Cell) to 10^7 CFU/g (deep Nitrate Cell), with Core 2-2 falling within this range. Counts in the pristine sample were greater than in three of the four contaminated samples (Figure 4-10). However, a response to gasoline contamination was indicated by clearly-discernable differences in colony types between the pristine- and contaminated-sample plates. Denitrifiers ranged from 4×10^3 MPN/g in the pristine sample to $>2 \times 10^6$ MPN/g in the deep sample from the Nitrate Cell. Samples from the Nitrate Cell contained the highest numbers of denitrifiers. Benzene-toluene degraders were less prolific, with numbers ranging from 4×10^1 MPN/g in the pristine sample to 7.5×10^3 MPN/g in the deep sample from the Nitrate Cell.

The numbers of culturable microorganisms in the samples extracted from the treatment cells were slightly higher than the pristine sample from Core 2-2. Both denitrifiers and benzene-toluene degraders were higher by up to two orders of magnitude, but differences in aerobic heterotrophs were less pronounced. The largest numbers for all three groups were observed in the Nitrate Cell, possibly indicating a response to NO_3^- application. However, it should be noted that the number of samples collected from the treatment cells was too small to characterize the variability within these affected areas. If one considers all of the enumeration results in pristine aquifer material (Table 4-9), numbers of aerobic heterotrophs and denitrifiers were quite variable, and it is less clear that numbers in contaminated regions were elevated. This may indicate that the

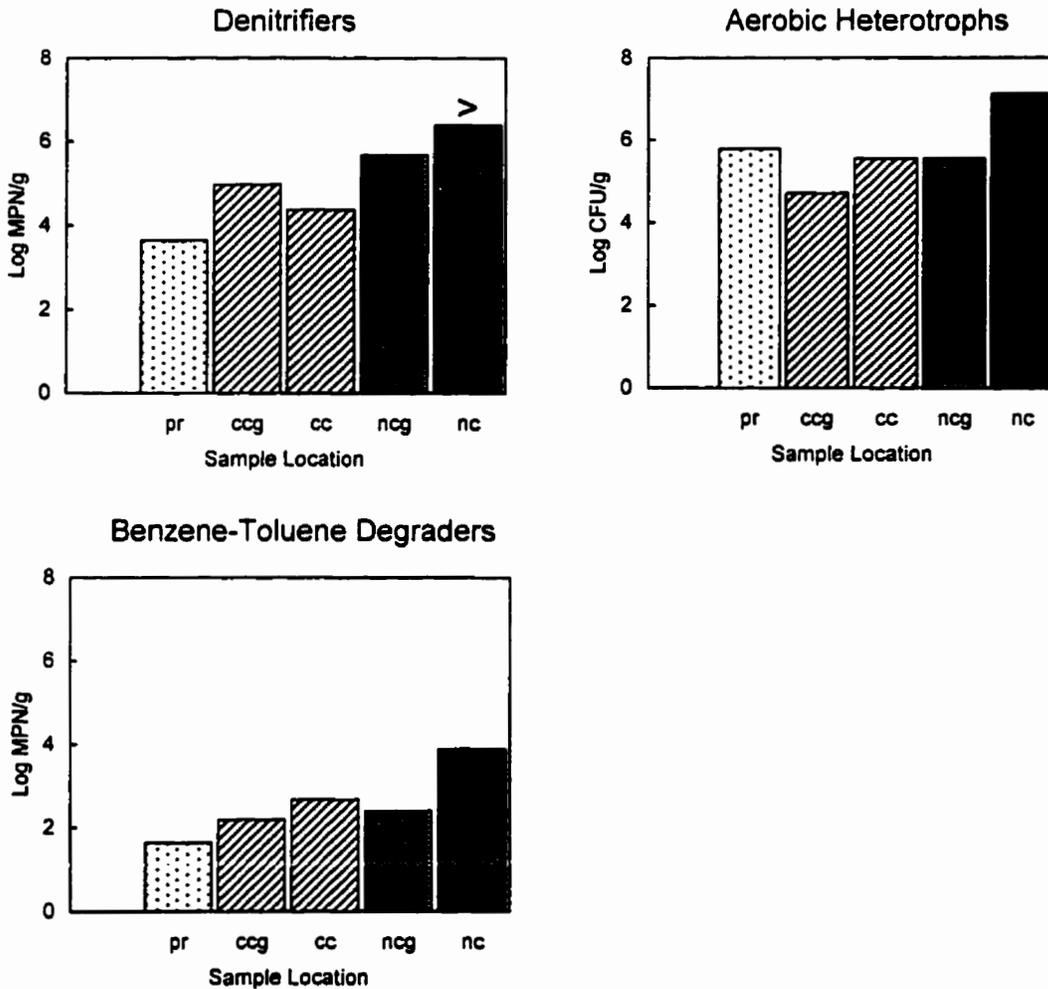


Figure 4-10. Numbers of denitrifiers, aerobic heterotrophs, and benzene-toluene degraders in pristine and contaminated aquifer material. pr: pristine (Core 2-2); ccg and ncg: samples from gasoline-contaminated zones in Control and Nitrate Cells, respectively; cc and nc: samples from below gasoline-contaminated zones in Control and Nitrate Cells, respectively. ">" = greater than 2×10^6 MPN/g of denitrifiers in ncg replicates.

dominant hydrocarbon-degrading population was not enumerated by the culture techniques used here. On the other hand, similar numbers are consistent with *in situ* electron-acceptor and organic-substrate utilization data which suggested that electron-acceptor flushing did not stimulate the growth of a large degrading population.

Dehydrogenase Activity. The ETS-activity assay was performed to compare aerobic microbial activity in pristine and contaminated aquifer material. This test has the potential to represent a larger fraction of the indigenous population than cell counts because it provides a direct measurement of the total activity in the aquifer material (Barbaro et al., 1994). The treatment groups are summarized in Table 4-10. Because of dilution with other fluid, the actual aqueous hydrocarbon concentrations in the vials were roughly half the gasoline-contacted concentrations (ca. 50 mg/L and 5 mg/L total aromatics). For consistency with the enumerations, these vials were incubated at room temperature. Dehydrogenase activity was assayed in samples of pristine aquifer material (Core 2-2), the zones below the gasoline contamination (155-190 cm bgs) in both treatment cells, and the gasoline-contaminated zone (80-140 cm bgs) of the Nitrate Cell.

Table 4-10. Experimental design: ETS activity in pristine and contaminated aquifer material.

Treatment	Hypovial Contents
Blank	Borden aquifer solids, water, N,P
Sterile	Autoclaved Borden aquifer solids, INT, 0.5 ml sodium azide, water N,P
Unamended	Borden aquifer solids, INT, water, N,P
Positive	Borden aquifer solids, INT, 0.5 ml glucose, water, N,P
Gasoline-saturated	Borden aquifer solids, INT, 1 ml gasoline-saturated water, water, N,P
1/10 gasoline-saturated	Borden aquifer solids, INT, 1 ml 10x dilution of gasoline-saturated water, water, N,P

Each treatment was prepared in duplicate and incubated under aerobic conditions.

Blank-corrected INT-formazan production is shown in Figure 4-11. For clarity data are plotted as means of duplicate determinations, but for some samples there was substantial variability between duplicates. Trends based on means provided, therefore, only an approximate measure of differences in activity. Activity varied by both sample location and amendment. The largest accumulation of INT-formazan occurred in the deep sample from the Nitrate Cell when gasoline-saturated water was supplied as a carbon source (Figure 4-11). Activity in the deep sample from the Control Cell was similar, except that INT-formazan accumulation in the gasoline-saturated vials was substantially lower. In both of these samples, substantial activity also occurred in unamended vials, which probably reflects utilization of existing gasoline hydrocarbons. In the Control Cell, activity in the positive (glucose-amended) treatment was similar to the unamended treatment, but in the Nitrate Cell, it was much greater. It is not clear why the positive controls behaved differently. Activity was generally lower in the pristine sample, but surprisingly, accumulations over the 28-day incubation in the treatments amended with gasoline-saturated water were greater than those in the positive control which contained an easily-utilized carbon source. Again, as in the Control Cell, it is not clear why the activity in the glucose-amended vials was low. The lowest activities occurred in the sample collected from the gasoline-contaminated zone in the Nitrate Cell. Therefore, the gasoline phase seemed to suppress ETS activity somewhat relative to the other contaminated sample locations included in this experiment.

Overall, on the basis of a limited number of samples, this assay indicated that ETS activity was affected by gasoline exposure. In general, the greatest activity in the presence of gasoline-saturated water occurred in the lower samples collected from the treatment cells. The overall highest ETS activity was observed in the Nitrate Cell. Although activity as measured by this assay was relatively low in the presence of a gasoline phase, there was other evidence that the aerobic population, and hence the potential for aerobic biotransformation of aromatic hydrocarbons, was not completely suppressed within the gasoline source area (Experiment 3).

4.4 Discussion and Conclusions

The effect of microaerophilic dissolved O₂ concentrations was found to depend primarily on the amount of substrate in the microcosms. When the concentration of aqueous aromatic hydrocarbons was low (i.e., on the order of 10-15 mg/L) and there were no other sources of labile

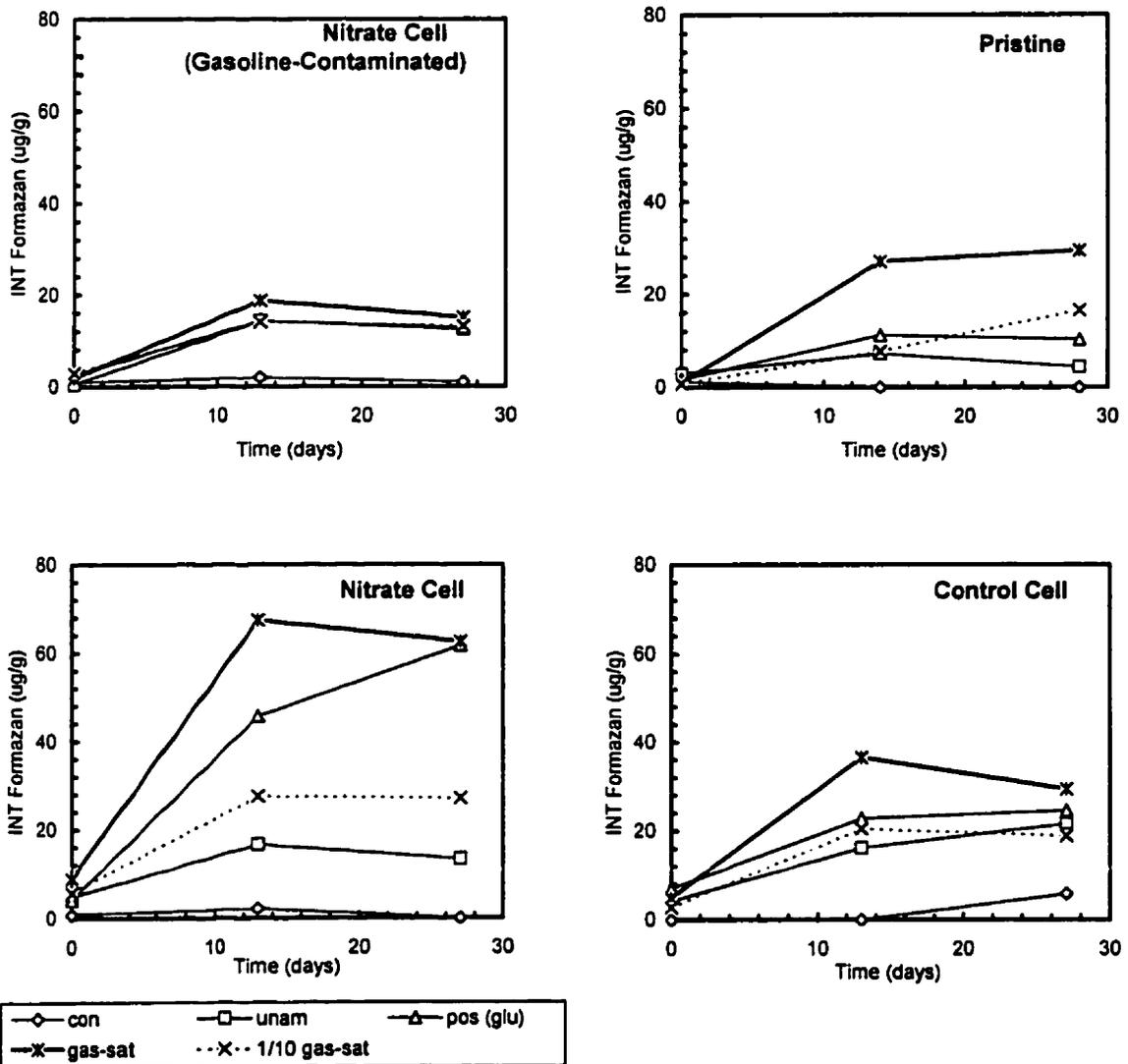


Figure 4-11. Accumulation of INT Formazan as a measure of ETS activity in pristine and contaminated aquifer material. Results shown in bottom two graphs from below gasoline-contaminated zones. con: sterile control; unam: no carbon source added; pos: glucose added; gas-sat: gasoline-saturated water added; 1/10 gas-sat: 10x dilution of gasoline-saturated water added. Means of two replicates plotted.

carbon (pristine aquifer material), the mass of O₂ in a microcosm was fairly large relative to the mass of carbon. For example, Experiment 1 showed that under these conditions, the mass of O₂ derived from an air headspace was sufficient to mineralize roughly half of the mass of aromatic hydrocarbons in a microcosm. Notably, however, benzene losses were minimal in these microaerophilic microcosms.

In microcosms prepared with gasoline-contaminated aquifer material, on the other hand, less extensive losses of the aromatics were observed in the presence of microaerophilic O₂, even when aqueous hydrocarbon concentrations were low. This apparently was the result of O₂ consumption by microorganisms growing on other carbon compounds. Abiotic O₂ consumption in laboratory microcosms appeared minor. Other carbon compounds that may have been labile include non-target aqueous gasoline constituents such as phenolic compounds (see Table 5-2) and various C₄ through C₇ straight-chained aliphatic compounds which have relatively high aqueous solubilities, or various insoluble hydrocarbons in the gasoline phase. Microorganisms capable of assimilating insoluble hydrocarbons by various means have been identified in many previous studies (Marin et al., 1996; Alexander, 1999). When the concentrations of aqueous aromatic hydrocarbons were increased to gasoline-saturated concentrations to reflect field conditions, microaerophilic O₂ had no observable effect. Under these conditions, the mass of O₂ was apparently too low to observe any losses even if the aromatic hydrocarbons were utilized as preferred substrates. Therefore, although there was an observable effect under favorable conditions (i.e., low substrate concentrations in pristine aquifer material), microaerophilic O₂ was not effective in enhancing the removal of recalcitrant compounds under conditions similar to those established in the field. These laboratory data suggest that the addition of microaerophilic O₂ for enhanced bioremediation may be more effective in locations downgradient of the source.

Complete utilization of microaerophilic O₂ was not observed in laboratory microcosms. A threshold dissolved O₂ concentration of 0.1-0.5 mg/L persisted in active microcosms incubated in the anaerobic chamber. It is unclear whether this threshold resulted from positive sampling bias (i.e., removal of the microcosms from the anaerobic chamber prior to D.O. analysis), or was representative of the microcosm liquid. In contrast to the field cells, where threshold concentrations were also observed, laboratory samples were not subjected to negative pressure prior to sampling and steps were taken to minimize contamination with atmospheric O₂ prior to

measurement (Appendix C). Nonetheless, in this study, it was assumed that the threshold represented the lowest measurable concentration, and microcosms with O₂ concentrations near this level were considered to be O₂-depleted. Assuming, on the other hand, that this residual O₂ was not an experimental artifact, the data suggested that microbial consumption was very slow relative to the lengths of the incubation periods. Persistence could have been related to slow kinetic uptake at these concentrations (Section 1.3.1). The effects, if any, on the denitrifier population could not be determined, but continued NO₃⁻ depletion was observed after the apparent threshold had been reached. The presence or absence of a threshold concentration, while of interest for understanding the fate of supplied O₂, did not appear to be critical in the assessment of the effect of microaerophilic O₂.

Although one of the objectives of this study was to evaluate nitrate-based biotransformation, the laboratory experiments clearly showed that aromatic-hydrocarbon mass losses were minor in the absence of O₂. In pristine aquifer material, NO₃⁻ utilization was observed under anaerobic conditions, but only when aromatic-hydrocarbon concentrations were low (10x dilution of gasoline-contaminated groundwater). Under these conditions, mass losses were limited to toluene and ethylbenzene. When aqueous concentrations were increased to gasoline-saturated levels, negligible NO₃⁻ utilization suggested that denitrifying activity was completely inhibited in pristine aquifer material. Prolonged (19 months) *in situ* exposure to gasoline hydrocarbons and NO₃⁻ did lead to increased NO₃⁻ utilization under anaerobic conditions. Although denitrifying activity was apparently occurring in these gasoline-contaminated microcosms, however, losses of the labile aromatic hydrocarbons were generally very minor. As discussed previously, this may simply reflect a preference for other organic substrates, such as other gasoline hydrocarbons or their metabolites. Lower utilization of aromatics in the presence of multiple substrates has been observed in other studies with hydrocarbon-contaminated aquifer material (Hutchins et al., 1991a). In contrast, benzene, toluene, ethylbenzene, *m*-xylene, *p*-xylene, 1,2,4-trimethylbenzene, and naphthalene were observed to biotransform rapidly in the gasoline-contaminated material at the expense of O₂. *o*-Xylene and the other trimethylbenzene isomers may also have been degrading at lower rates, but they were effectively recalcitrant because of rapid O₂ consumption in other reactions.

Nitrate may have been involved in both assimilatory and dissimilatory reactions. Indirect evidence of assimilatory reduction in gasoline-contaminated material was provided by the rapid utilization of NO_3^- in the presence of a large mass of O_2 (Figure 4-5a). If this NO_3^- utilization had resulted from denitrifying activity following significant aerobic growth of facultative microorganisms, and other factors such as production of toxic byproducts were not limiting reactions, then rapid utilization of NO_3^- should have continued under anaerobic conditions. Subsequent rapid utilization after NO_3^- replenishment was not observed. Utilization of NO_3^- as a source of N for O_2 -driven reactions can be considered a positive aspect of an $\text{O}_2 / \text{NO}_3^-$ mixture, but under microaerophilic conditions the effect would be limited. Under anaerobic conditions, the intermittent accumulation of NO_2^- as well as the production of N_2O in acetylene-blocked microcosms suggested that dissimilatory NO_3^- reduction had been induced, but these data were variable and the specific NO_3^- -reducing pathway remained unclear. The rate and extent of NO_3^- utilization were also quite variable among the different treatment groups in this experiment. This inconsistent NO_3^- -reducing activity appears to be a characteristic response in laboratory studies with Borden aquifer material.

In contrast to other published studies, the laboratory experiments performed in this study provided no clear evidence that low levels of O_2 were facilitating the continued transformation of recalcitrant compounds such as benzene under anaerobic, denitrifying conditions (Hutchins, 1991c). Similarly, there was no evidence from substrate disappearance curves (i.e., greater mass losses than those expected from mineralization reaction stoichiometries) that microaerophilic O_2 was being utilized to partially-oxidize the aromatic hydrocarbons. Previous experiments with low substrate concentrations did show, however, that mass losses of labile compounds in mixed microaerophilic / NO_3^- microcosms exceeded losses in comparable microaerophilic only, and anaerobic, denitrifying microcosms (Barbaro et al., 1998). These experimental results suggested that denitrifying activity commenced after O_2 depletion with no apparent lag period, and that total biotransformation losses were maximized by the presence of two electron acceptors. Unfortunately, in the Borden aquifer enhanced mass loss under mixed electron-acceptor conditions appeared to occur only when the concentrations of the labile substrates were low. These results are broadly consistent with those obtained *in situ*.

With *in situ* exposure the microbial community in the Borden aquifer appeared to adapt to the gasoline phase and associated high aqueous-concentrations of the aromatic hydrocarbons. As indicated previously, distinct differences were observed in the utilization of O₂, NO₃⁻, and the aromatic hydrocarbons in microcosms containing pristine and contaminated aquifer material. For instance, despite relatively little *in situ* exposure to O₂, microcosm data showed that aerobic aromatic-hydrocarbon degrading activity was very robust following 19 months of gasoline exposure. On the other hand, the limited amount of enumeration data was less indicative of a major response to gasoline contamination; these data were more consistent with other field observations which suggested that flushing did not stimulate the growth of a large degrading population. There were also indications (e.g., ETS activity) that aerobic microbial activity was suppressed somewhat in the presence of a gasoline phase. Overall, however, the laboratory work indicated that aerobic biotransformation in the gasoline source area would have been beneficial after a period of exposure.

CHAPTER 5. FIELD EXPERIMENT

5.1 Overview of Results

5.1.1 Flow Characteristics

All breakthrough curves (BTCs) within the pea gravel layers (60 cm bgs) reached a relative concentration near $C/C_0=1$ within 12 hour of the beginning of the July, 1996 tracer test (Appendix B). Because the pea-gravel layers extended to the sheet-piling walls, it is likely that injected water spread horizontally to the edges of the cells throughout the flushing experiments, providing a uniform initial distribution of NO_3^- and dissolved O_2 , although the apparent rapid consumption of O_2 may have restricted its initial distribution to the region around the injection well.

Breakthrough data from piezometer ports at two depths, 120 and 180 cm bgs, were used to calculate dispersivities and groundwater velocities (Appendix B). As the tracer front migrated downward through the cells, spatial groundwater velocity fluctuations were observed, but tracer was detected at all monitored ports; this indicated that there were no large regions of the cells that had been bypassed by the injected fluid. Velocity fluctuations in individual flow tubes were likely caused by spatial variability in the hydraulic gradient (i.e., higher velocities above the extraction well), in aquifer properties such as hydraulic conductivity (heterogeneities), and in gasoline content. Average linear groundwater velocities, determined from fitting a one-dimensional advection-dispersion equation to the tracer BTCs, ranged from 0.6 to 1.2 cm/hr in the Control Cell, and 0.4 to 1.1 cm/hr in the Nitrate Cell (see Table B-2).

The velocities measured from breakthrough data can be compared to the expected velocity under steady flow conditions. Using a porosity of 0.33, a 200 ml/min target injection rate yields an expected velocity of 0.9 cm/hr, which is consistent with the breakthrough data. Accordingly, the mean injection flow rates were used in advective mass-flux calculations to estimate the masses of aqueous constituents added and removed from the cells under flushing conditions. The good agreement between injection rates and breakthrough data also indicated that there was no short-circuiting of injected water along the walls of the piezometers.

5.1.2 Dissolved Oxygen and Nitrate

Dissolved Oxygen. Dissolved O₂ depletion was observed in both treatment cells. The mean injection dissolved O₂ concentrations were 2.3±1.8 mg/L (n=80) and 2.3±1.7 mg/L (n=81) for the Nitrate and Control Cells, respectively, where the variability is expressed as a standard deviation. These means include the initial seven days of the experiment when fully-oxygenated water was injected into the cells. If the measurements from the first week are excluded, mean injection concentrations fall to 1.9±0.9 mg/L and 2.0±1.0 mg/L for the Nitrate and Control Cells, respectively. The mean concentrations obtained from 13 samples collected from the extraction-well sampling ports were 0.30±0.14 mg/L (Nitrate Cell) and 0.27±0.26 mg/L (Control Cell). Measured concentrations are shown on Figure 5-1, where a mean value is plotted when more than one sample was collected in a 24 hr period. The amount of O₂ injected into the cells is calculated in Appendix E.

Dissolved O₂ was depleted rapidly to a non-zero threshold concentration in both cells (Figure 5-2). Concentrations in samples from 60-cm ports were at the threshold, and additional utilization between 60- and 180-cm depths was not observed. Therefore, the majority of the dissolved O₂ was utilized within hours of injection. The threshold concentration varied from about 0.4 mg/L to 1 mg/L, depending on the location, and averaged around 0.75 mg/L at a given depth interval (Figure 5-2). Threshold concentrations were also measured during both the static and 24-day flushing periods that followed the initial flushing experiment (Appendix F). It appears, based on rapid rates of utilization in active laboratory microcosms relative to controls (e.g., Microcosm Experiment 3), that O₂ was utilized primarily by microbial activity, but it could not be determined whether the aqueous aromatic hydrocarbons or other gasoline constituents were serving as substrates. Also, given the detection of dissolved Mn in water extracted from the supply well (Table 2-1), it is possible some of the O₂ was utilized in abiotic reactions as well.

The observed threshold concentrations obtained from the piezometers may not represent *in situ* dissolved-O₂ concentrations. One possible source of positive bias is the sampling procedure (Figure 3-8). A small amount of O₂ could have been incorporated into the flowing stream of groundwater during sampling under suction. To further investigate this possibility, similar sampling techniques were used to measure the dissolved O₂ concentrations from a group of bundle

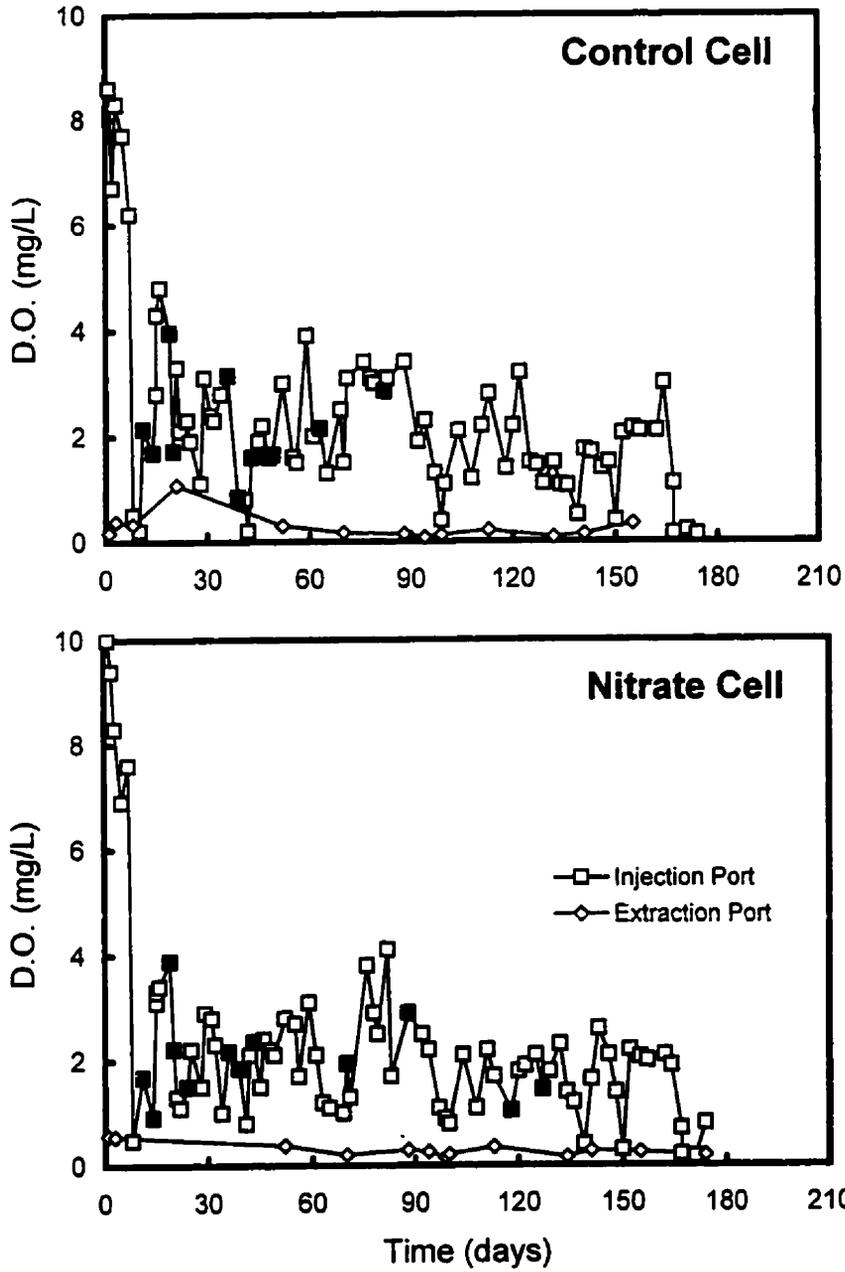


Figure 5-1. Injection and extraction D.O. concentrations. Mean values plotted when more than one sample collected within 24-hr period (solid squares).

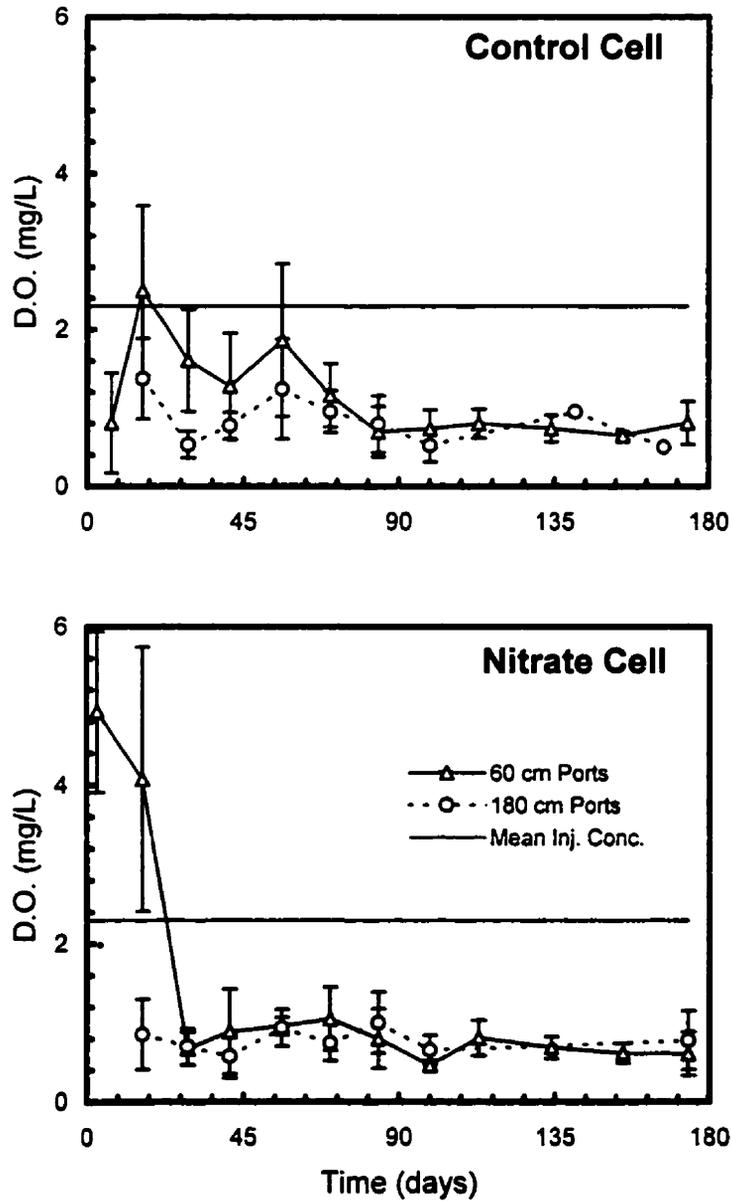


Figure 5-2. D.O. concentrations at 60- and 180-cm bgs ports during the 174-day flushing experiment. Plotted values at each depth are means and standard deviations from five piezometer ports.

piezometers located in the anaerobic, landfill leachate plume (Barbaro et al., 1992). Mean concentrations of duplicate samples from seven piezometer ports ranged from 0.4 mg/L to 0.9 mg/L. This suggested that contamination with atmospheric O₂ did occur during sampling. Another test was performed to compare D.O. data from the extraction well in the Nitrate Cell with data obtained from selected ports on the adjacent piezometer, PZ4E. As shown in Figure 5-3, although these data were obtained from similar depths in the cell, D.O. concentrations from all of the piezometer ports were higher than concentrations obtained from the extraction well. On the other hand, vertical profiles from center piezometers indicated that dissolved O₂ concentrations decreased progressively during the flushing experiments (Figure 5-4). Concentrations lower than the threshold values discussed above were obtained on the last sampling date when the cells were static, suggesting that it was possible to measure lower O₂ concentrations from these ports. Because of these inconsistencies, the dissolved O₂ data obtained from the multilevel piezometers were considered semi-quantitative; they showed that dissolved O₂ was essentially removed, but could not be used to define the actual residual concentration. Samples from the extraction wells may be considered more representative of *in situ* conditions, but these data could also reflect minor contributions from groundwater in the underlying aquifer, and stagnant water in the well casing.

Nitrate. The mean injection NO₃⁻ concentration from the initial 174-day flushing experiment was 116±33 mg/L (n=25). The mean concentration from the extraction well port was 82±23 mg/L (n=13). Because there were two target injection concentrations (Figure 5-5), the means and standard deviations were calculated as described in Section 3.4.3 for injection rates. Nitrate was not detected in the Control-Cell injection water (n=3).

Consumption of NO₃⁻ under flushing conditions was relatively low. Similar to dissolved O₂, NO₃⁻ depletion during the 174-day experiment appeared to occur rapidly after injection into the cell (Figure 5-6). Mean concentrations from 60-cm ports were below injection concentrations, but additional losses between 60 and 180 cm depths appeared to be quite small (Figure 5-6). Mean concentrations also show the similarity between NO₃⁻ data crossing these planes. The overall mean concentrations for the 174-day flushing experiment were 105±19 mg/L (n=11) and 105±11 mg/L (n=11) from the 60-cm and 180-cm ports, respectively. In this calculation each data point used to calculate the temporal mean was itself a spatial mean of the concentrations from each of the five

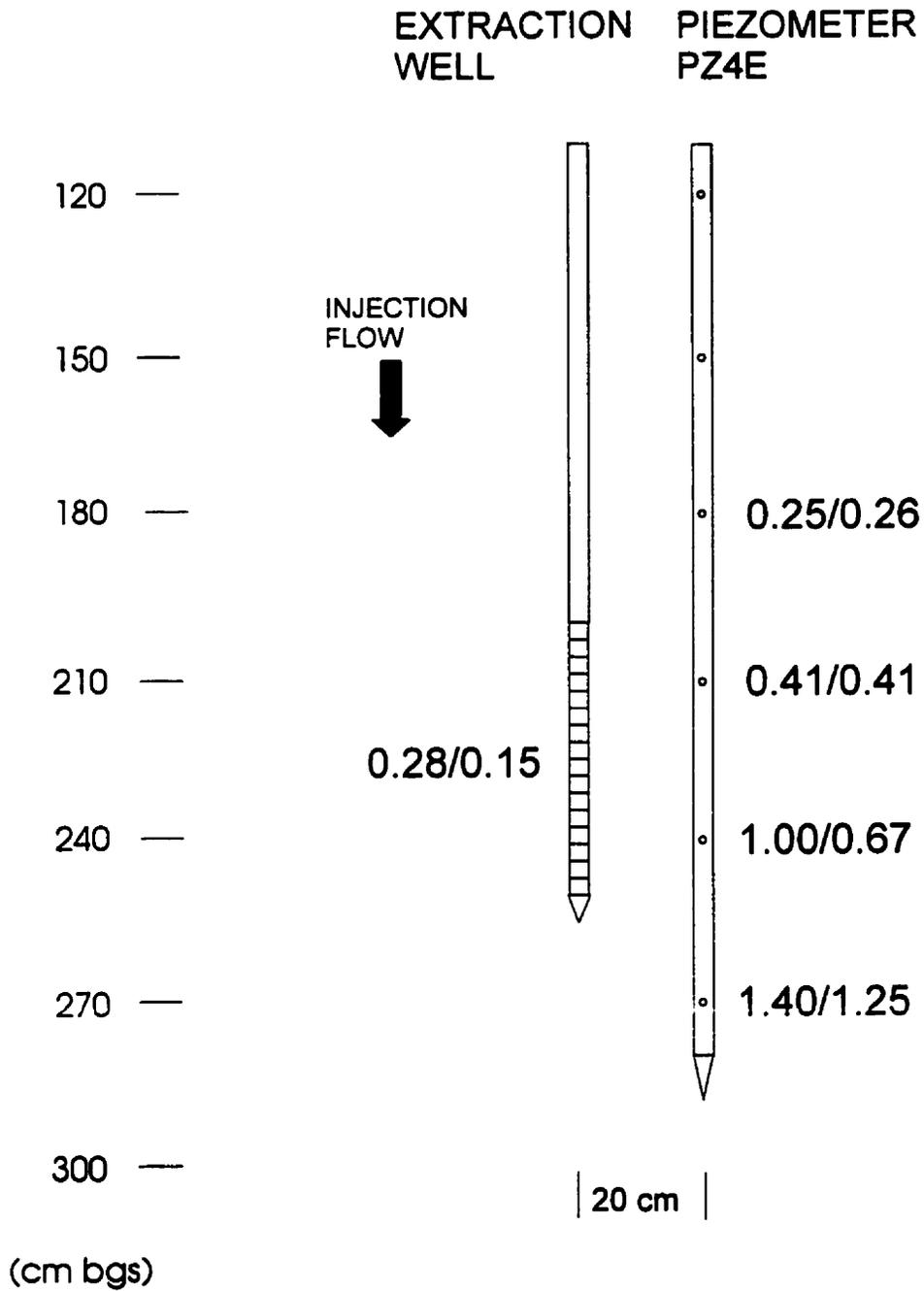


Figure 5-3. Dissolved O₂ concentrations (mg/L) collected from the extraction well and the adjacent multilevel piezometer in the Nitrate Cell during July, 1996 when the flushing experiment was in progress. Two samples were collected successively from each location.

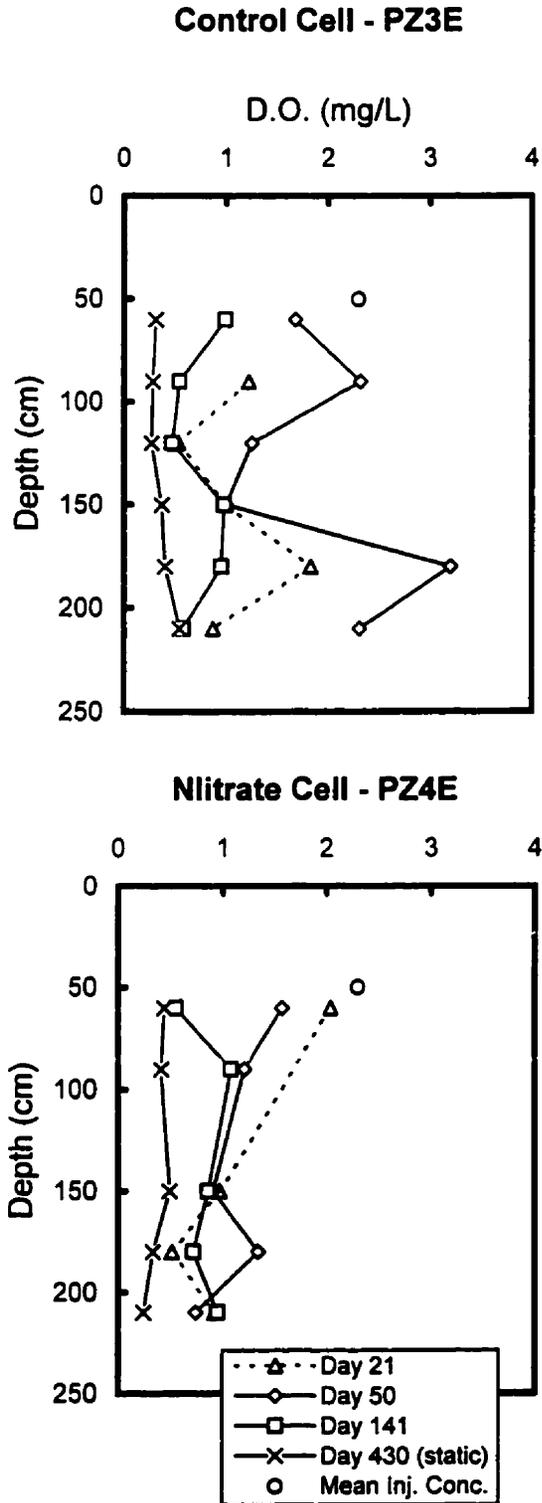


Figure 5-4. Vertical profiles of D.O. at various times during and after the 174-day flushing experiment. Data collected from center piezometers.

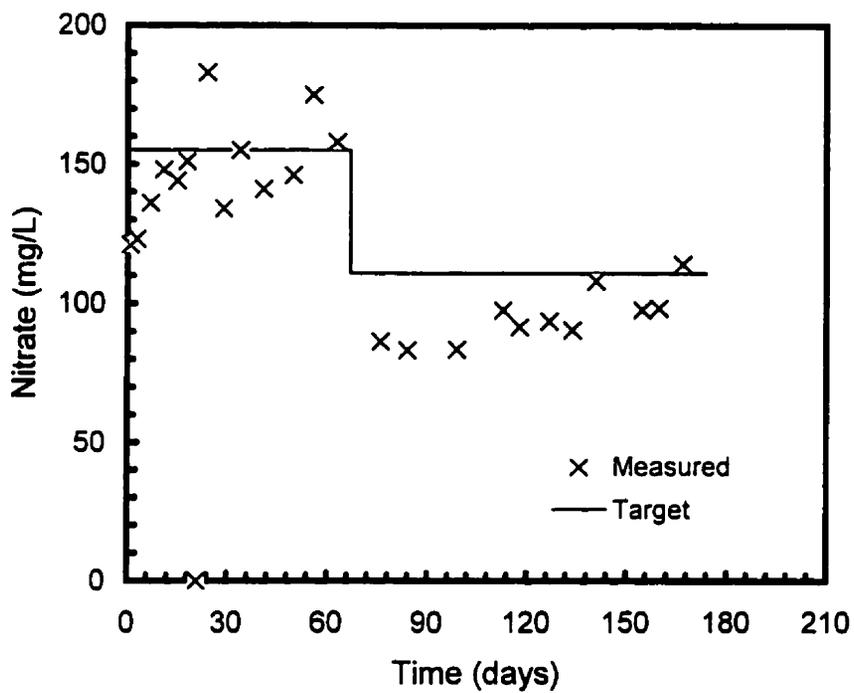


Figure 5-5. Injection NO_3^- concentrations.

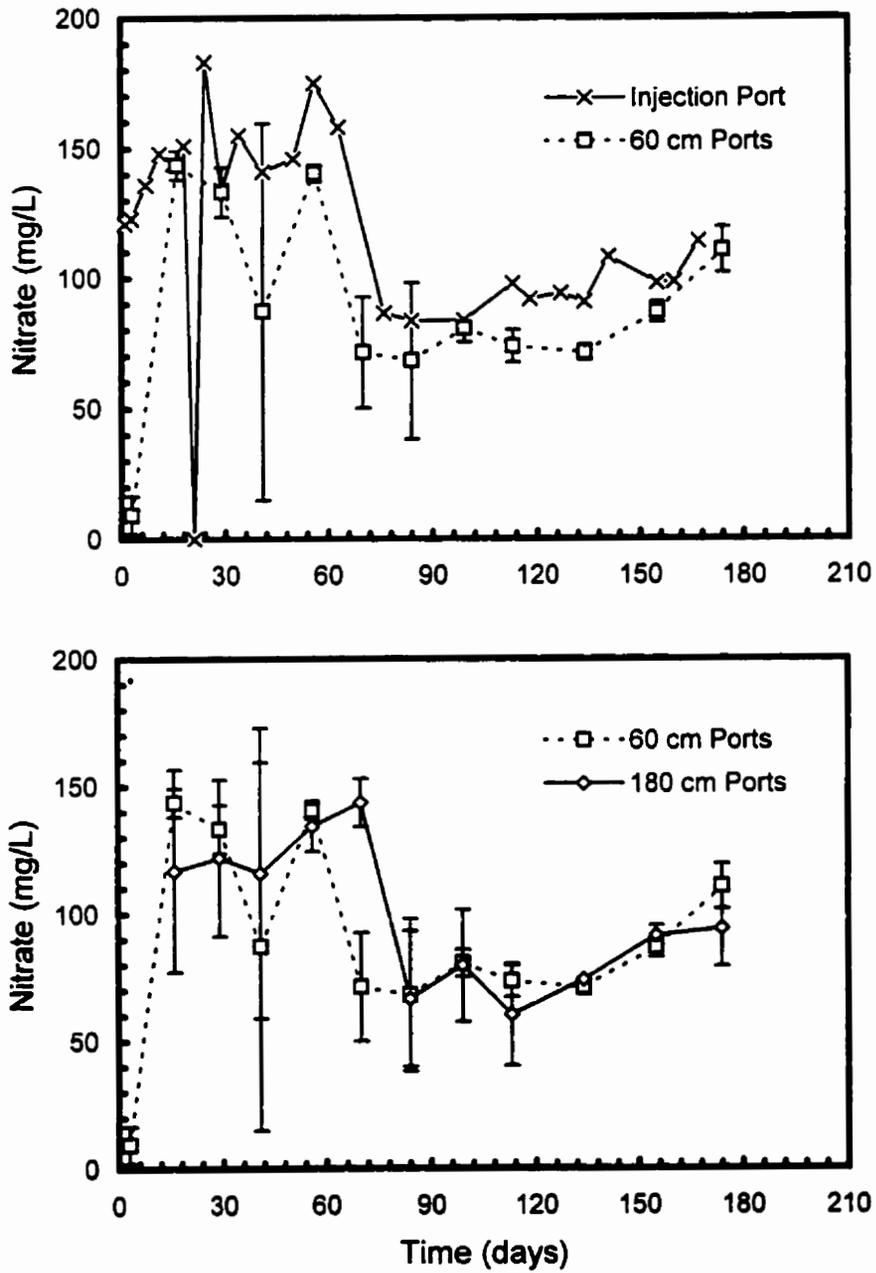


Figure 5-6. Nitrate concentrations in injection water and 60- and 180-cm bgs ports during the 174-day flushing experiment. Plotted values for 60- and 180-cm depths are means and standard deviations from five piezometer ports.

sampling port at that depth (e.g., Figure 5-6), and the calculations were performed as described in Section 3.4.3.

Similar behavior was observed during the 24-day flushing experiment. The addition of the MBH medium during this 24-day period did not result in an observable increase in the rate of NO_3^- utilization. This result was consistent with previous laboratory experiments (e.g., Barbaro et al., 1998), which have indicated that denitrifying activity in the Borden aquifer is not nutrient limited. The amount of NO_3^- that was utilized during the 174-day flushing experiment is calculated in Appendix E.

To determine if NO_3^- utilization would be observed during a longer residence time, a conservative tracer (bromide) was pumped into the Nitrate Cell during the final week of the 174-day flushing experiment. Three ports from the 60-cm depth and three from the 180-cm depth were then sampled over the following 138 days when the cells were static to observe the extent of anaerobic NO_3^- depletion relative to Br^- . However, depletion of both Br^- and NO_3^- was observed, particularly at the lower depth where dilution with underlying groundwater may have occurred in response to a rising water table. To account for depletion of the tracer, Br^- concentrations from each sampling port were corrected back to the initial concentration. These correction factors were then applied to the corresponding NO_3^- value to obtain a corrected concentration for each sampling event. A mean corrected NO_3^- concentration was then calculated from the three ports at each depth for each sampling event (Figure 5-7). While there is substantial scatter in the data, this figure indicates that there were losses of NO_3^- relative to Br^- , with greater losses at the lower depth. If depletion is described with a zero-order (linear) model, depletion rates of 0.20 mg/L/d (60 cm) and 0.67 mg/L/d (180 cm) are obtained. Given the scatter in the data, a first-order model could also be fit reasonably well to the data. These fits yielded first-order rate constants of $k=0.002/\text{d}$ (60 cm) and $k=0.02/\text{d}$ (180 cm). As discussed further in the following sections, these trends have been attributed to biological activity.

5.1.3 Organics

Aqueous-Phase. As shown by effluent data, aqueous aromatic-hydrocarbon concentrations were quite high in both cells (Figure 5-8). By the end of the flushing experiments, concentrations

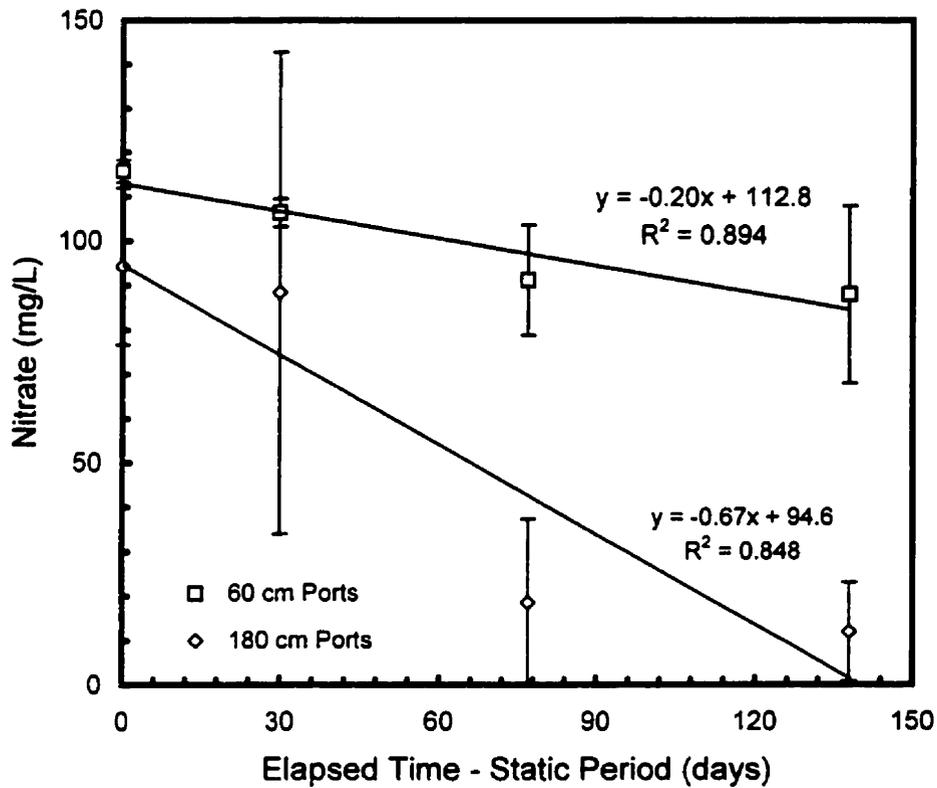


Figure 5-7. Nitrate concentrations during the static period between flushing experiments. Bromide was used to correct NO_3^- concentrations as discussed in text. Plotted values at each depth are means and standard deviations from three piezometer ports.

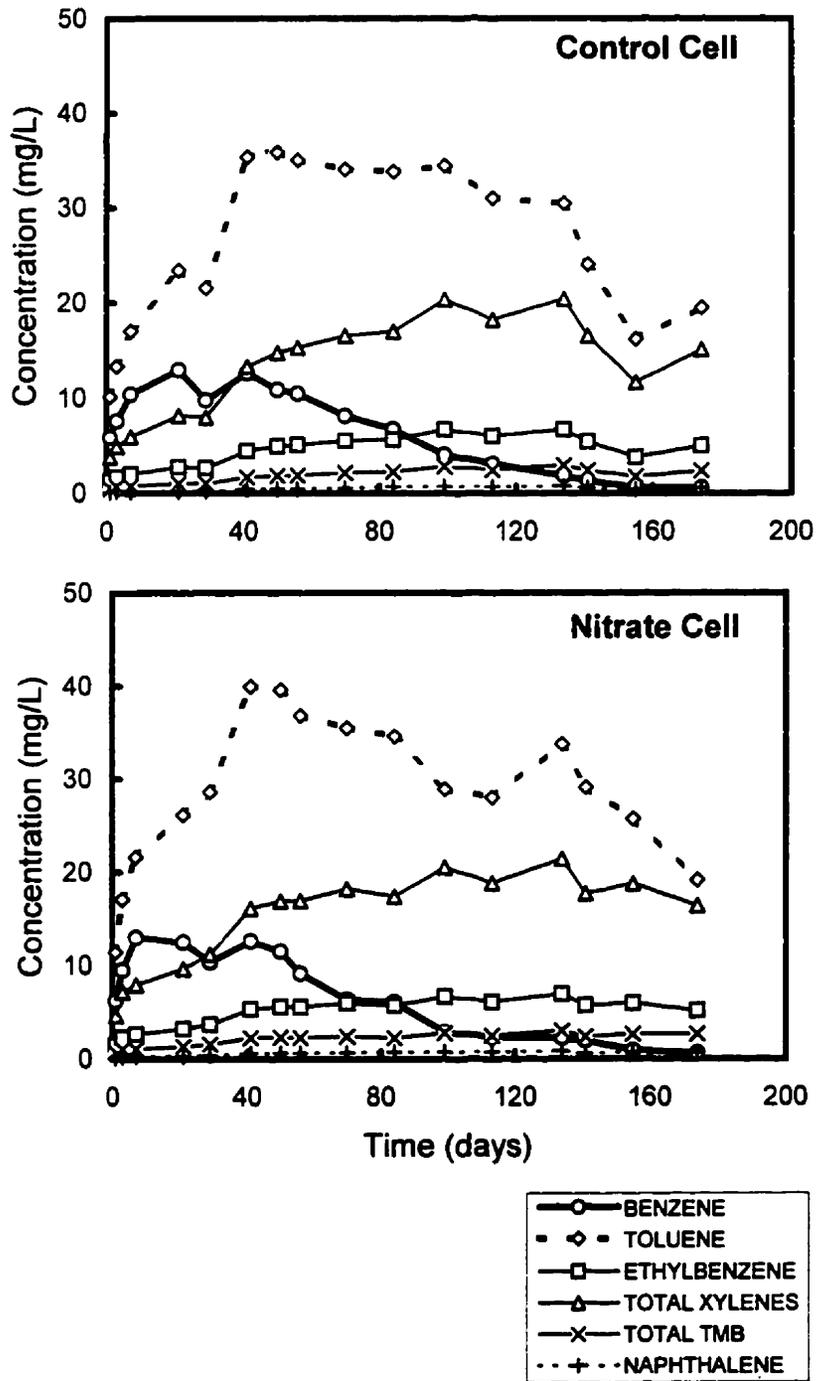


Figure 5-8. Concentrations of dissolved aromatic hydrocarbons in samples collected from extraction-well ports.

ranged from about 1 mg/L for benzene to 20 mg/L for toluene. With the exception of benzene and toluene, final concentrations in effluent water were similar to their respective concentrations in gasoline-saturated water, as measured in laboratory equilibration experiments with fresh API 91-01 (see Table A-4). Benzene and toluene concentrations declined to ca. 5% and 50% of initial gasoline-saturated values, respectively, reflecting rapid changes in the mole fractions of these constituents. In contrast, after about 2 months of flushing, concentrations of the less soluble compounds (i.e., xylenes, trimethylbenzenes and naphthalene) reached initial saturated values and remained at these levels throughout the experiment. The reasons for the relatively slow approach to equilibrium concentrations are not clear. One possible explanation is that dilution with uncontaminated water was more extensive during the early stages of flushing. Another possibility is that, despite attempts to locate the extraction wells above the peat layer, organic-rich deposits located near the base of the treatment cells substantially decreased solute migration velocities. These concentration trends are shown for the Nitrate Cell in Figure 5-9, and discussed in more detail in Section 5-4.

Relatively rapid depletion of the more soluble compounds is consistent with the dissolution of a multi-component organic liquid. As indicated by these aqueous results, the gasoline phase was nearly depleted in benzene, but not in the less-soluble aromatics, by the end of the experiment (Figures 5-8 and 5-10). The rapid depletion of benzene was expected on the basis of its high solubility, and was consistent with equilibrium partitioning between the gasoline and mobile groundwater. The vertical profiles shown in Figure 5-10 suggest that benzene was depleted most rapidly from the top of the gasoline-contaminated region, and that the depleted zone propagated downward as flushing progressed. Other relatively-soluble compounds such as toluene showed similar trends. The relatively rapid removal of the soluble constituents is also evident from 180-cm BTCs (Figures 5-11 and 5-12).

The temporal and spatial patterns of aqueous concentrations were also quite similar between cells (Figures 5-8 through 5-12). Based on a visual inspection of the 180-cm BTCs, there were no major differences between the cells in the patterns of aqueous aromatic hydrocarbons (Figures 5-11 and 5-12). For example, preferential removal of toluene, the most labile compound under denitrifying conditions, was not evident in the Nitrate Cell relative to the Control Cell. Despite potential differences in the degree of dilution from the underlying aquifer, similarities

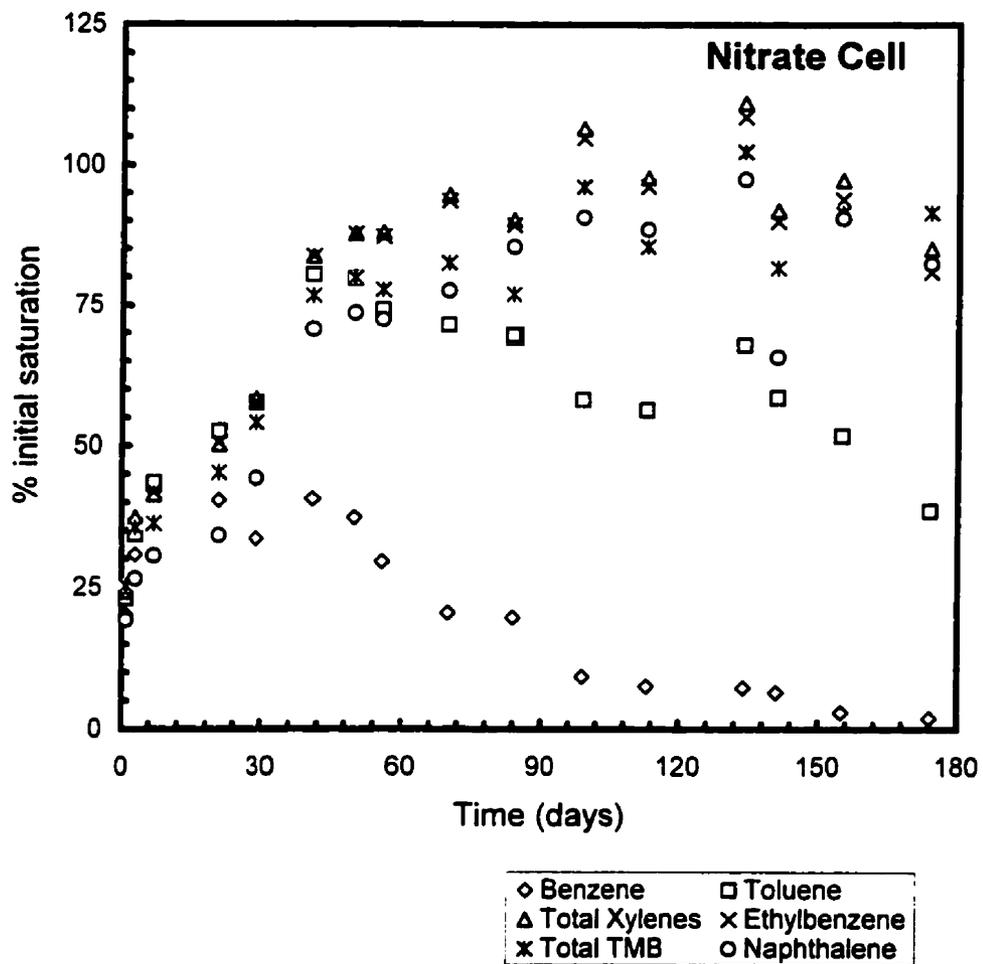
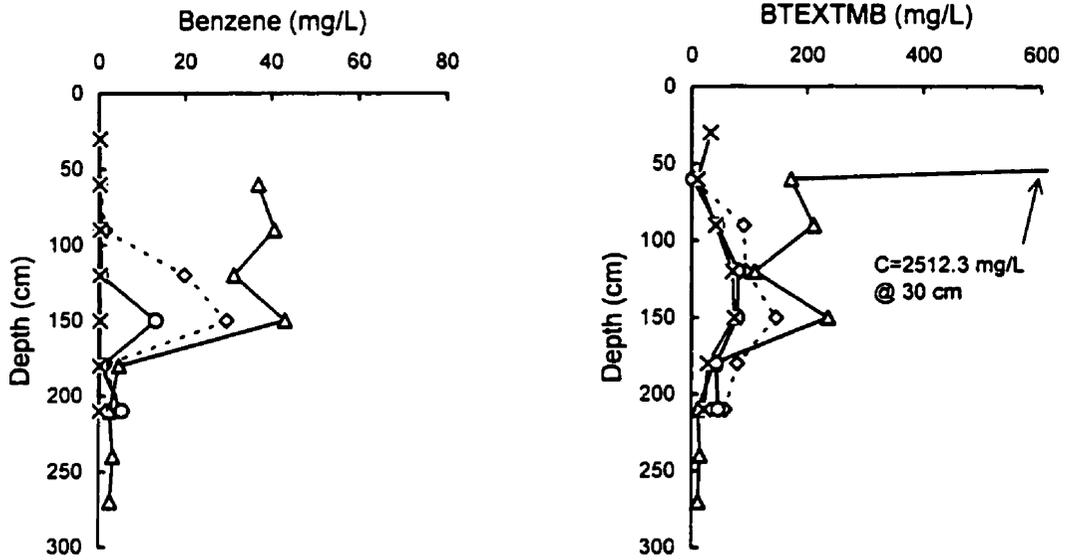


Figure 5-9. Concentrations of aromatic hydrocarbons in samples collected from the extraction-well expressed as percentages of concentrations in water equilibrated with fresh API 91-01 gasoline.

Control Cell



Nitrate Cell

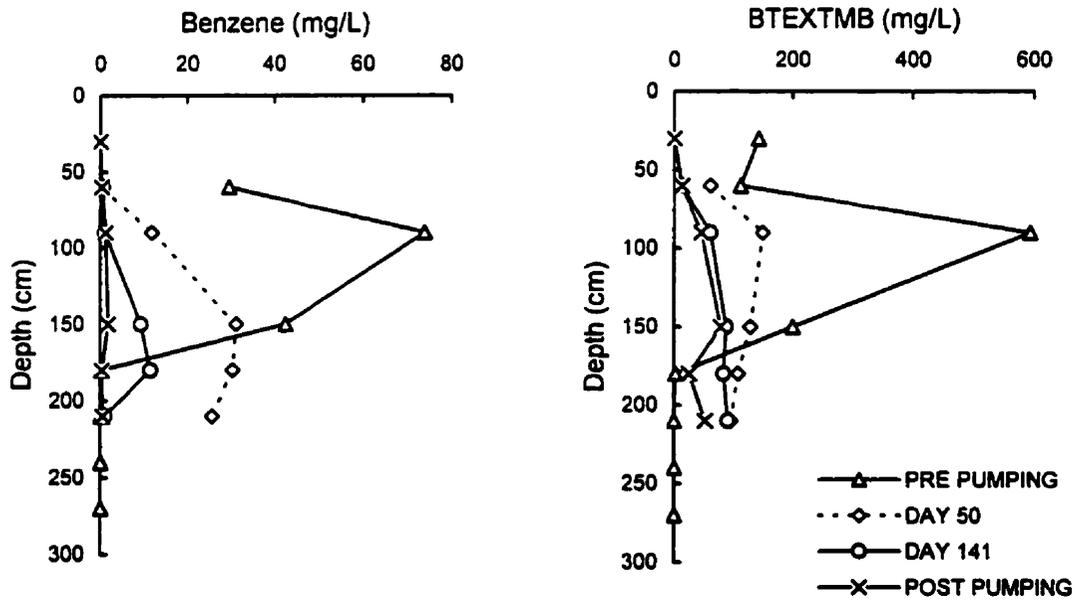


Figure 5-10. Vertical profiles of benzene and total BTEXTMB before, during, and after the flushing experiments. Data collected from center piezometers.

Nitrate Cell - 180 cm Depth

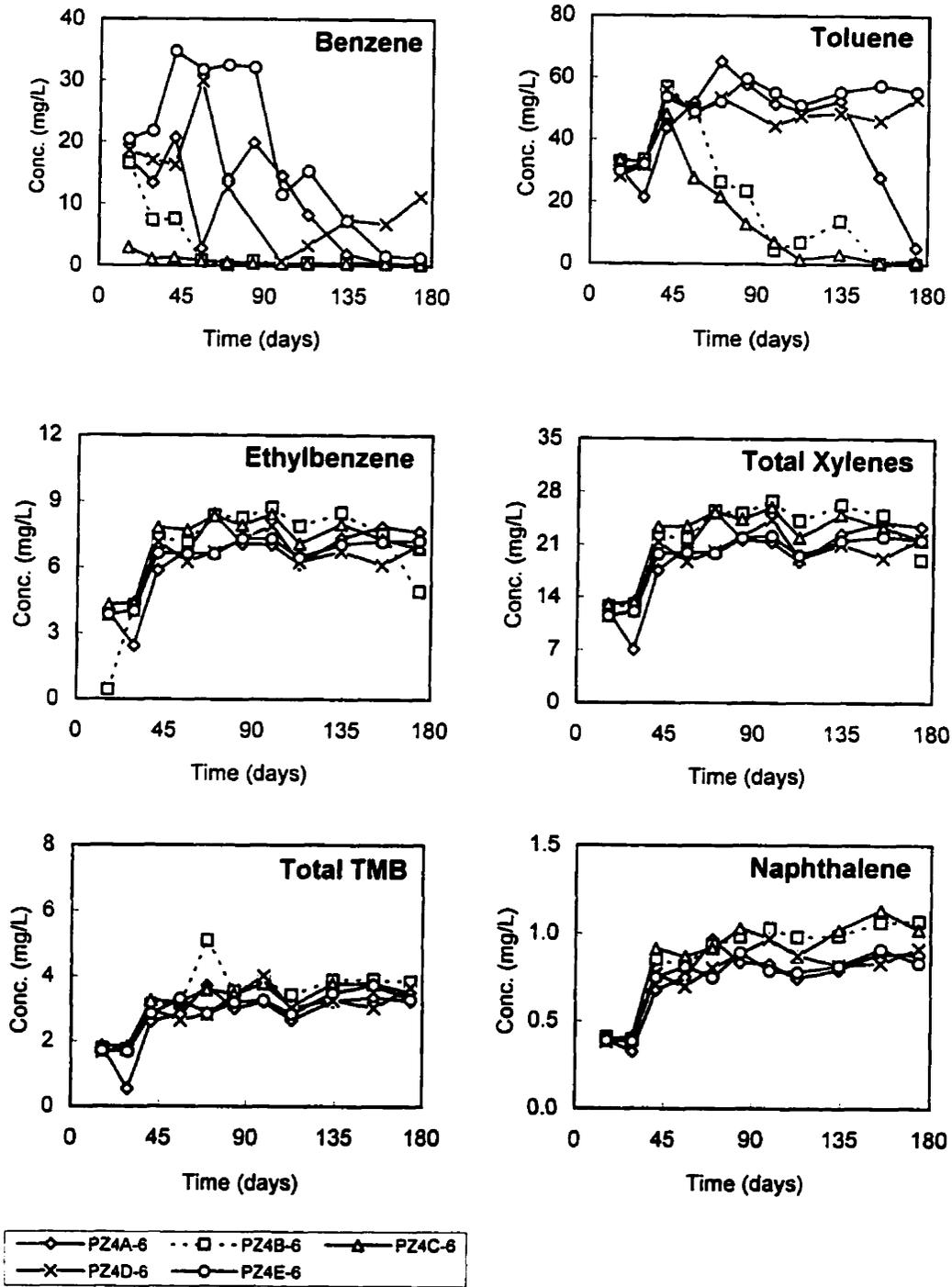


Figure 5-11. Concentrations of dissolved aromatic hydrocarbons at individual 180-cm bgs ports in the Nitrate Cell during the 174-day flushing experiment.

Control Cell - 180 cm Depth

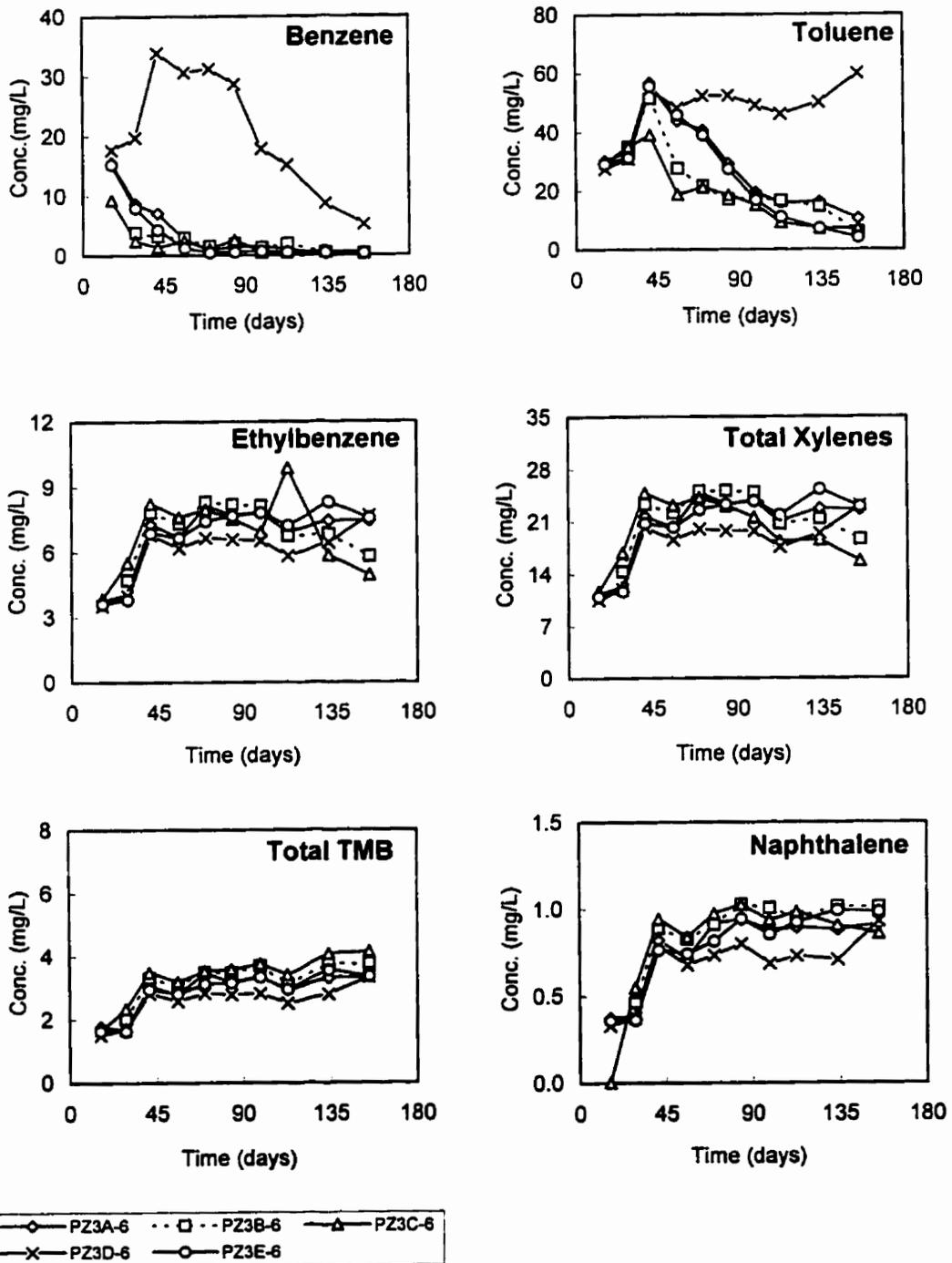


Figure 5-12. Concentrations of dissolved aromatic hydrocarbons at individual 180-cm bgs ports in the Control Cell during the 174-day flushing experiment.

between the cells are also apparent in the extraction-well BTCs (Figure 5-8). In terms of average effluent concentrations, means of total BTEXTMB over both flushing periods (199 days) were 56 ± 14 mg/L (Nitrate Cell) and 51 ± 15 (Control Cell) for $n=19$ samples. Means of individual compounds were similar as well. The close similarity of the Nitrate- and Control-Cell breakthrough curves is additional evidence that a common, abiotic transport process such as dissolution was the dominant mass removal mechanism.

Concentrations of aromatic hydrocarbons did not decline appreciably in either cell during the static period between flushing experiments. This includes compounds such as toluene and ethylbenzene that are typically labile in the Borden aquifer under anaerobic, denitrifying conditions (e.g., Barbaro et al., 1992). The apparent lack of aromatic-hydrocarbon utilization in the Nitrate Cell is important because NO_3^- depletion was observed during this period. Figure 5-13 shows toluene, ethylbenzene, and NO_3^- from one of the piezometers (PZ4A) that was sampled during the static period. Concentrations were corrected for declining Br^- as described in Section 5.1.2. These plots suggest that if NO_3^- was being used by denitrifying bacteria as an electron acceptor, the labile aromatic hydrocarbons did not serve as the preferred substrates.

Core Extracts. The distribution and quantity of aromatic hydrocarbons remaining in the cells after the flushing experiments were completed was estimated from core extract samples. Concentrations of total BTEXTMB ranged from below detection limits to about 6,000 mg/kg of aquifer material (Figure 5-14 and 5-15). On the basis of a visual inspection, patterns between cells were remarkably similar. Peak concentrations show that the gasoline-contaminated zones were located within the 50 to 150 bgs depth interval. This pattern is consistent with the aqueous profiles shown in Figures 3-5, 3-6, and 5-10. With the exception of cores 3K and 4L, located near the centers of the cells where the gasoline phase was deeper, all cores transected the entire gasoline-contaminated interval. Highest concentrations of residual aromatic hydrocarbons were present in the center of the cells and in the upper right quadrants (Figures 5-14 and 5-15). As with the aqueous phase, concentrations of individual compounds in the residual gasoline phase were broadly consistent with trends expected to result from gasoline dissolution, i.e., the residual gasoline was most depleted in soluble compounds such as benzene and toluene.

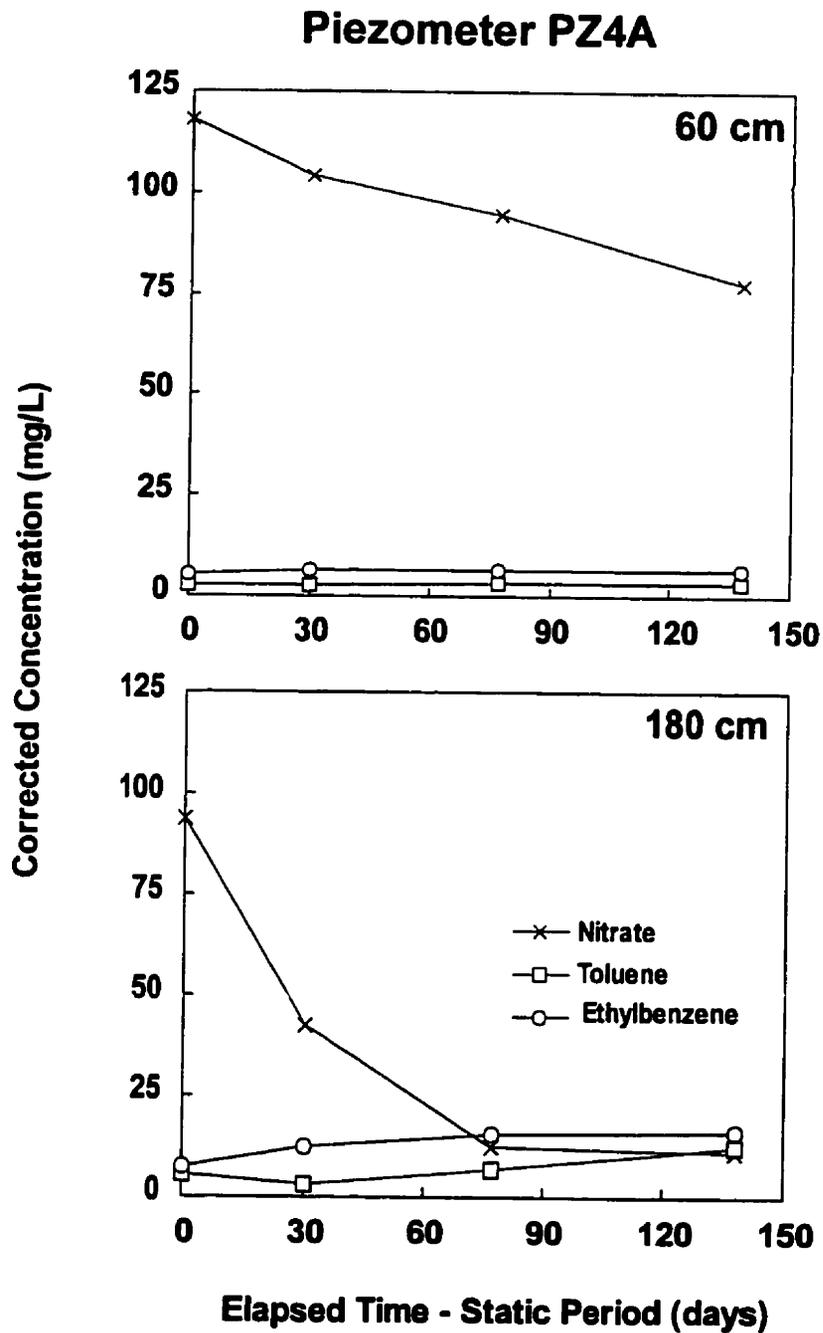


Figure 5-13. Corrected toluene, ethylbenzene, and NO_3^- concentrations from a selected piezometer in the Nitrate Cell that was sampled during the static period. Upper graph: 60-cm bgs port; Lower graph: 180-cm bgs port. Bromide was used to correct concentrations as discussed in text.

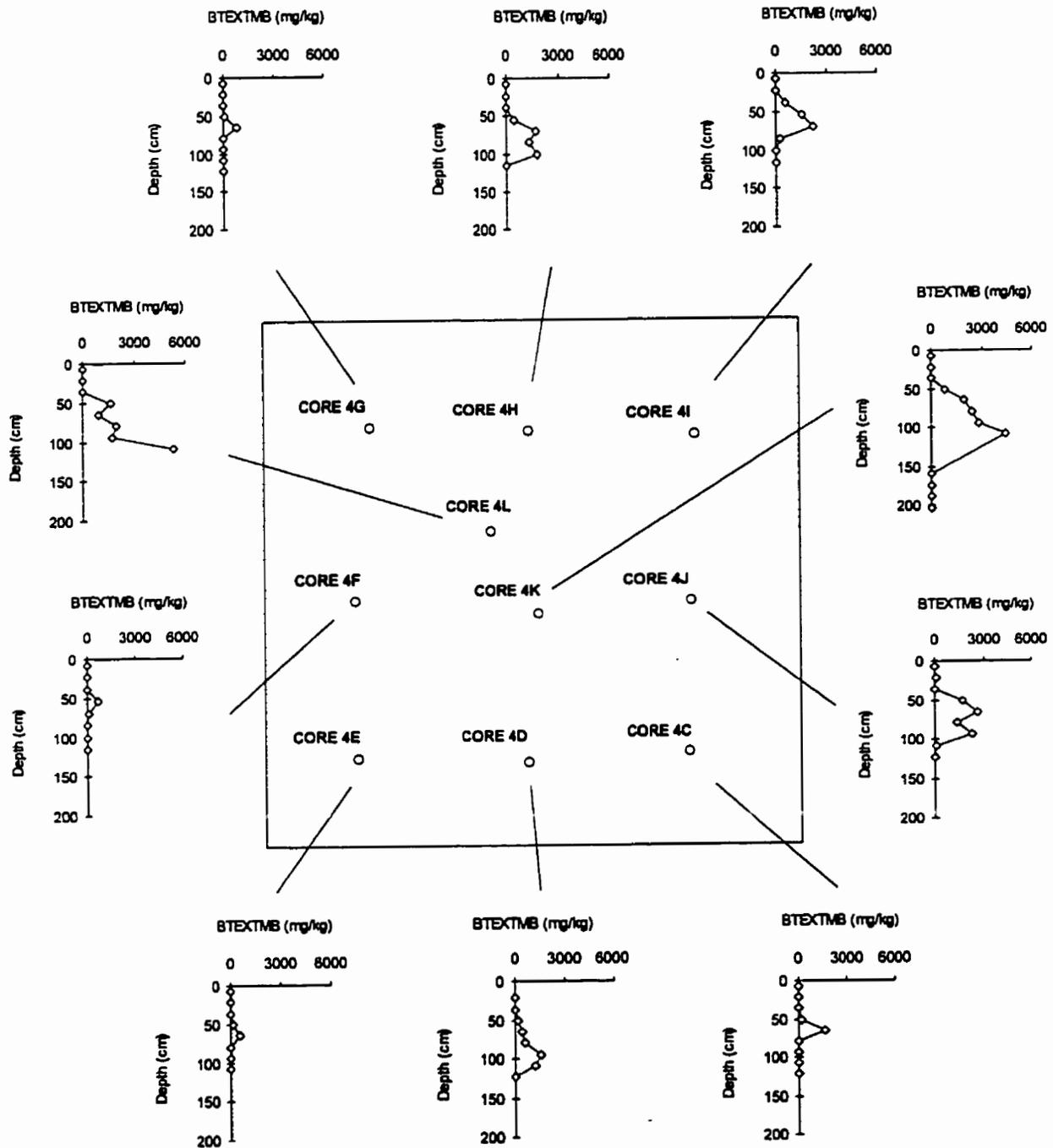


Figure 5-14. Vertical profiles of residual BTEXTMB in the Nitrate Cell. Concentrations obtained from field methanol extraction of core subsamples. Cores were collected during August, 1997. Surveyed core locations also shown.

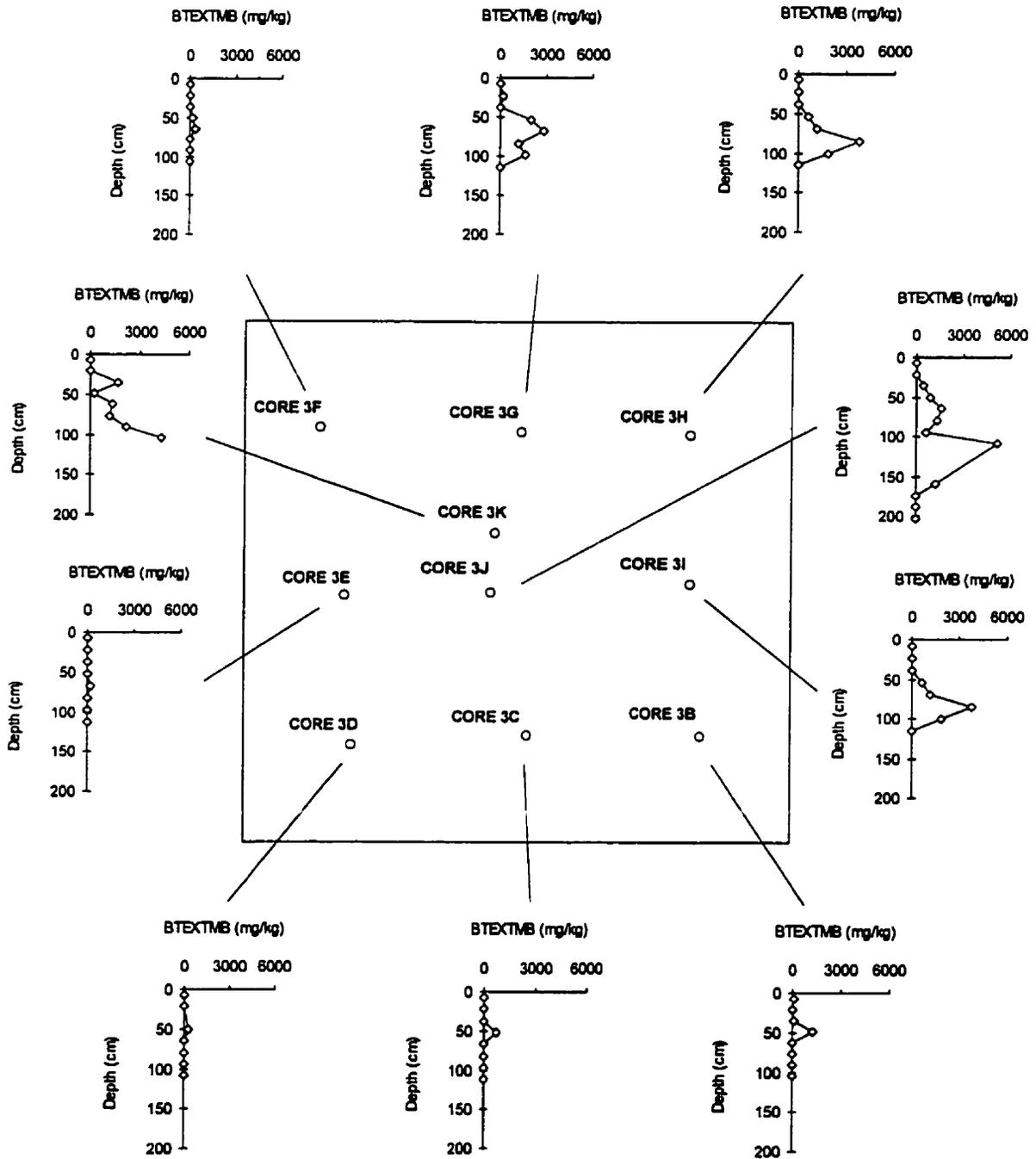


Figure 5-15. Vertical profiles of residual BTEXTMB in the Control Cell. Concentrations obtained from field methanol extraction of core subsamples. Cores were collected during August, 1997. Surveyed core locations also shown.

To further examine concentration differences, a paired t-test was also performed on the concentration data from the cells. Because concentrations appeared to be highly correlated by location, differences between maximum concentrations from cores in the same location relative to the gasoline injection well (e.g., Cores 3B and 4C) were first calculated. The sample of differences (n=10) was then tested to determine whether the mean difference was significantly different than zero at the $\alpha=0.05$ level of significance. For each compound, the normality of the sample of differences was verified with a probability plot. For all compounds, there was insufficient evidence to reject the null hypothesis of no difference (p=0.58 (toluene) to p=0.99 (1,2,3-TMB)). This result is consistent with the graphical presentation of the data. It is important to note that because the field treatments were unreplicated, the experiment was not controlled for among-replicate random variability, initial variability between the experimental units (i.e., treatment cells), or intrusion of chance events during implementation (Hurlbert, 1984). As a consequence, the statistical test used here can only measure concentration differences between these two locations; had a significant difference been observed, it could not have been attributed to the application of NO_3^- . Other evidence would be required to establish a causal relationship.

With the exception of Core 4I which appeared to be depleted in alkanes, the analysis of core extracts for gasoline component classes did not reveal substantial depletion of any hydrocarbon component group relative to the fresh gasoline standard and sample spiked with fresh API 91-01 (Table 5-1). This was consistent with the short duration of the flushing experiments and the low solubilities of the majority of the gasoline constituents.

5.1.4 Nitrite Production

Nitrite was frequently present in groundwater samples collected from the Nitrate Cell. Nitrite was never detected in samples of injection water spiked with NO_3^- , but was present in 70% of the groundwater samples (n=189), collected under both flushing and static conditions, that contained NO_3^- (Appendix F). Concentrations were typically less than 1 mg/L as NO_2^- , but there were numerous occurrences between 1-10 mg/L, and the highest measured concentration was 17.2 mg/L as NO_2^- . In general, NO_2^- was detected more frequently and at higher concentrations in samples collected from lower depth intervals. The presence of NO_2^- is considered evidence of dissimilatory NO_3^- reduction (Mikesell et al., 1993). Nitrate can be reduced to N_2 abiotically in

Table 5-1. Hydrocarbon component classes in API 91-01 gasoline and gasoline-contaminated core extract samples. Core samples collected July, 1997. All results expressed in weight percent.

Class	Depth (cm bgs):	API 91-01 Gasoline	Gasoline Spike	CONTROL CELL			NITRATE CELL		
				Core 3J 80	Core 3H 69	Core 3K 50	Core 4I 70	Core 4L 65	Core 4K 65
Alkanes		46.8	40.7	43.0	44.2	48.0	30.6	46.6	42.8
Aromatics		35.3	44.2	39.9	38.4	34.0	61.1	34.9	40.0
Bicycloalkanes		0.1	<0.1	nd	nd	nd	nd	nd	nd
Naphthenes		7.9	5.7	7.1	7.3	7.0	3.5	8.0	6.9
Olefins		6.6	5.6	5.4	5.7	5.5	0.7	5.3	5.9
PNA		0.5	0.2	0.5	0.7	0.7	nd	1.1	0.8
Other		2.9	3.6	4.1	3.8	4.8	4.1	4.1	3.7

nd - not detected

the presence of Fe^{2+} , but because the reaction rate is negligible unless pH is alkaline (i.e., >7), and a catalyst such as Cu is present (Buresh and Moraghan, 1976), it has been discounted as an important mechanism here.

5.1.5 Metabolite Production

Additional evidence of microbial activity was obtained from the presence of metabolites (Table 5-2). It is recognized that these samples were collected after the flushing experiments were completed, and the MBH medium had been pumped into the cells, and therefore may not be representative of earlier flushing conditions when the majority of the electron-acceptor utilization and aromatic-hydrocarbon mass removal occurred. However, because a response (i.e., changes in electron-acceptor and hydrocarbon utilization) to the MBH solution was not apparent, and concentrations of other redox-sensitive species were similar to those measured during flushing conditions (Table 5-3), it has been assumed that conditions at the time of metabolite sampling were representative of this earlier period.

The sample of fresh API 91-01 gasoline did not contain any aromatic or aliphatic acids. The supply well was sampled on two occasions, and several C_3 through C_5 aliphatic acids as well as benzoic acid were present in the supply water. This may indicate that a plume of partially-oxidized hydrocarbon constituents from the upgradient treatment mound had reached the supply well by the end of the experiment. Alternatively, short-chained aliphatic acids can be formed from the fermentation of natural organic matter in low- O_2 environments (Thurman, 1985; McMahon and Chapelle, 1991). Concentrations of the constituents detected in supply water were generally higher in the treatment cells, suggesting additional production within the cells. For example, although benzoic acid was detected at $5 \mu\text{g/L}$ in the supply well, it was present at concentrations up to $41 \mu\text{g/L}$ (PZ4E-3) in the Nitrate Cell, and $21 \mu\text{g/L}$ (PZ3E-3) in the Control Cell. Additional aliphatic and aromatic acids that were not detected in supply water or fresh gasoline were present in the treatment cells (Table 5-2). Groundwater in the Nitrate Cell contained alkyl-substituted benzoic acids at concentrations up to ca. $400 \mu\text{g/L}$ for 2,5-dimethylbenzoic acid. These compounds are structurally similar to the aromatic-hydrocarbon fraction of the gasoline, and although it could not be verified in this experimental system, their presence in the treatment cells

Table 5-2. Detected Organic acids and phenols in API 91-01 gasoline and groundwater. All concentrations in ug/L.

Compounds	Collection Date: Location: Depth (cm bgs):	NA Gasoline	NITRATE CELL				CONTROL CELL					
			6/12/97	7/30/97	6/12/97	7/30/97	6/12/97	7/30/97	6/12/97	7/30/97		
			Supply Well	Supply Well	PZ4E-2 60	PZ4E-3 90	PZ4E-6 180	PZ4E-6 180	PZ3E-2 60	PZ3E-3 90	PZ3E-6 180	PZ3E-6 180
Acetic acid			41		51		.		25		8	
Propanoic acid		.		7			6			7		..
2-methylpropanoic acid		32	50	11	1	..
3,3-dimethylpropanoic acid		.		..			10			5		5
trimethylacetic acid		..	.	14	.		22	.		28	14	37
butyric acid		..	2	4	66	..	1	..	10	10	.	..
2-methylbutyric acid		.	.	3	36	83	16	.	..
3-methylbutyric acid		..	.	4	48	234	34	.	..
3,3-dimethylbutyric acid			59		26		60		41		42	
pentanoic acid		..	.	3	75	..	11	..	23	3	80	..
hexanoic acid		.	.	5	16	7	3	5	.	9	.	
2-ethylhexanoic acid		2	..
2-methylhexanoic acid			8		10
heptanoic acid		14
benzoic acid		.	.	5	22	41	.	41	16	21	.	11
phenylacetic acid		71	7	.	12	126
o-methylbenzoic acid		.	.	.	218	8	3	21
m-methylbenzoic acid		.	.	.	83	17	.	5	.	28	.	7
m-tolyacetic acid	
p-tolyacetic acid		6	4	4
p-methylbenzoic acid		5	.	8
2,6-dimethylbenzoic acid		.	.	.	26
2,5-dimethylbenzoic acid		.	.	.	409	16	3	11
3,5-dimethylbenzoic acid		29	5
2,4-dimethylbenzoic acid		37	6	.	4
decanoic acid		18	3	.	..
4-ethylbenzoic acid	
2,4,6-trimethylbenzoic acid		.	.	.	99	4
3,4-dimethylbenzoic acid		.	.	.	14	6	.	5

Table 5-2. Detected Organic acids and phenols in API 91-01 gasoline and groundwater. All concentrations in ug/L.

Compounds	Collection Date: Location: Depth (cm bgs):	NA Gasoline	NITRATE CELL				CONTROL CELL					
			6/12/97	7/30/97	6/12/97	7/30/97	6/12/97	7/30/97	6/12/97	7/30/97		
			Supply Well	Supply Well	PZ4E-2 60	PZ4E-3 90	PZ4E-6 180	PZ4E-6 180	PZ3E-2 60	PZ3E-3 90	PZ3E-6 180	PZ3E-6 180
2,4,5-trimethylbenzoic acid		•	•	•	53/57	7	•	4	•	•	•	**
Phenol		44,000	•	•	•	4	•	•	4	•	•	•
o-cresol		53,800	•	•	•	7	•	•	•	•	•	•
m-cresol		37,600	•	•	•	5	•	•	•	•	•	•
p-cresol		19,000	•	•	•	•	•	•	•	•	•	•
o-ethylphenol		9,600	•	•	•	•	•	•	•	•	•	•
2,6-dimethylphenol		1,400	•	•	•	•	•	•	•	•	•	•
2,5-dimethylphenol		10,700	•	•	•	•	•	•	•	•	•	•
2,4-dimethylphenol		5,600	•	•	•	•	•	•	•	•	•	•
3,5-dimethylphenol + m-ethylphenol		24,900	•	•	•	9	•	•	•	•	•	•
2,3-dimethylphenol		5,500	•	•	•	•	•	•	•	•	•	•
p-ethylphenol		6,000	•	•	•	•	•	•	•	•	•	•
3,4-dimethylphenol		4,700	•	•	•	•	•	•	•	•	•	•

Samples collected on 6/12/97 analyzed by National Center for Integrated Bioremediation and Development, University of Michigan, Ann Arbor, MI

Samples collected on 7/30/97 and API 91-01 gasoline sample analyzed by National Risk Management Research Laboratory, U.S. EPA, Ada, OK

• - Not found.

** - Concentration of extract was below lowest calibration standard (3 ug/L)

Table 5-3. Concentrations in mg/L of selected redox-sensitive constituents in the experimental cells and injection water. Concentrations obtained during the flushing periods are expressed as a range of measured values. Concentrations from 3/22/97 and 6/12/97 sampling dates are from a single piezometer sample in each cell.

Sampling Interval: # Days:	Injection Water		Nitrate Cell			Control Cell		
	(5/96 - 11/96) 174	(5/97) 24	(5/96 - 11/96) 174 flushing	(3/97) 1 static	(6/97) 1 static	(5/96 - 11/96) 174 flushing	(3/97) 1 static	(6/97) 1 static
pH	6.84 - 7.48 ⁽³⁾	7.56	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Alkalinity (CaCO ₃)	252 - 269 ⁽³⁾	n.a.	248 - 267 ⁽⁸⁾	n.a.	n.a.	252 - 277 ⁽⁸⁾	n.a.	n.a.
Sulfate	2.05 - 9.07 ⁽⁷⁾	4.04	3.13 - 9.47 ⁽¹³⁾	1.70	4.14	2.65 - 10.6 ⁽¹⁶⁾	2.23	4.78
Sulfide	n.d.	n.a.	n.d. ⁽²⁾	n.d.	n.d.	n.d. ⁽⁴⁾	n.d.	n.d.
Total Iron	n.d. - 0.29 ⁽⁸⁾	2.37	n.d. - 0.12 ⁽¹³⁾	0.28	0.14	n.d. - 0.10 ⁽¹⁶⁾	0.34	1.30
Methane	1.04	n.a.	n.a.	1.47	0.46	0.24	0.94	0.088
Nitrate	n.d. - 175 ^{(25),a}	100 - 123 ^{(5),a}	n.d. - 160 ⁽¹⁸⁹⁾	10.6	88.9	n.d. ⁽¹³⁾	n.a.	n.a.
Nitrite	n.d. ^{(25),a}	n.d. ^{(5),a}	n.d. - 17.2 ⁽¹⁸⁹⁾	0.68	0.7	n.d. ⁽¹³⁾	n.a.	n.a.
Dissolved Oxygen	0.2 - 10.0 ⁽¹⁶¹⁾	3.9 - 5.6 ⁽⁸⁾		0.46	0.09		0.52	0.16

n.a. - Not analyzed

n.d. - Not detected. Detection limits provided in text.

⁽ⁿ⁾ - Number of samples collected during the indicated period.

^aNitrate Cell only.

All Samples in cells collected from various ports between 60- and 180-cm depths.

suggests that they were products of parent compounds in API 91-01. In other field studies alkyl-substituted benzoic acids have been related to alkylbenzene parent compounds (Cozzarelli et al., 1990; Cozzarelli et al., 1994).

The suite of compounds detected in the Control Cell was somewhat different. With the exception of *m*-methylbenzoic acid, samples from the Control Cell did not contain aromatic acids. This may represent lack of production of these compounds, or relatively rapid turnover to other oxidized constituents (Grbic-Galic and Vogel, 1987). There were, however, elevated concentrations of short-chained aliphatic acids (Table 5-2). The origin of these partially-oxidized compounds is less clear because of the numerous potential parent compounds in the gasoline.

The presence of low molecular weight organic acids derived from gasoline hydrocarbons demonstrates that, by the end of the flushing experiment, there was microbial activity in the treatment cells. The number of samples collected in this study was insufficient to determine whether these compounds resulted from aerobic or anaerobic transformations of gasoline constituents. However, production and persistence of these compounds has been observed frequently in anaerobic environments (Cozzarelli et al., 1990 (Fe-reducing and methanogenic); Kuhn et al., 1988 (NO₃⁻-reducing); Grbic-Galic and Vogel, 1987 (methanogenic)). In the Nitrate Cell, the redox potential of the system was probably buffered by the continuous presence of NO₃⁻ (Kehew and Passero, 1990). This suggests that acid production was most likely associated with NO₃⁻-reducing and/or O₂-reducing activity. In the Control Cell, the dominant terminal electron-accepting process is not known. Nitrate was not present, and periodic sampling for geochemical indicators of biotransformation did not provide evidence of substantial Fe-reducing, SO₄²⁻-reducing, or methanogenic activity. As shown in Table 5-3, ranges of SO₄²⁻ and total dissolved Fe in the Control Cell were similar to the supply water, as well as to the Nitrate Cell. Methane was present in both cells, but was also detected once in the supply-well water. The peat layer encountered at 2.8 m rather than gasoline hydrocarbons may have been the source of the CH₄ in these samples.

5.2 Mass Balance Results

Mass balances were performed on both added electron-acceptors and the aromatic hydrocarbons. Mass balance calculations along with the major assumptions made in the analysis are provided in Appendix E.

Because of the difficulties associated with obtaining reliable results from the multilevel piezometers, a rigorous mass balance was not performed on the dissolved O_2 . However, the mass injected into each cell was estimated using a simple mass flux calculation. The magnitude of the initial trapped air phase resulting from dewatering and gasoline emplacement was also estimated. Considering both sources of O_2 , the mass balance indicated that the total mass available for reactions may have been as high as ca. 300 g per cell. Based on the mass balance there was fairly minor utilization of NO_3^- under flushing conditions (Table 5-4). The estimated mass loss of 890 g represents only 12% of the NO_3^- pumped into the cell over the 174-day flushing experiment. Because there was substantial variability in the concentration data, it is possible that the calculated NO_3^- loss was an experimental artifact. The frequent detection of NO_2^- , however, suggests that at least some of the observed NO_3^- utilization was real (i.e., due to biological NO_3^- reduction). The NO_3^- mass loss results were consistent with observed changes in NO_3^- concentrations under both flushing and static conditions.

The mass balance on the aromatic hydrocarbons indicated that approximately 20% of the initial aromatic-hydrocarbon mass was lost between the gasoline spills and the coring exercise. This corresponds to roughly 2,500 g expressed as total BTEXTMB per cell (Table 5-5). It is important to note, however, that the analysis required several assumptions which may have systematically overestimated or underestimated the true mass in the treatment cells (Appendix E). This was particularly true for the estimates of the mass remaining in the gasoline-contaminated zone. Consequently, the absolute mass-loss amounts were not considered reliable, but because the net bias resulting from the analysis would have affected both cells in a fairly-uniform manner, the mass balance results were used to compare relative differences (or the lack thereof) between cell locations.

Table 5-4. Nitrate mass balance results for 174-day flushing experiment.

	Integrated Breakthrough Curve (mg/L*d)	(s.d.)	Injection Rate (L/d)	(s.d.)	Mass (g)	(s.d.)
INJECTED	19,791.4 ^a		360	(20.0)	7,130	(390)
EXTRACTED	17,323.4 ^b	(3,075.7)	360	(20.0)	6,240	(1,160)
MASS LOSS					890	(1,220)
MASS RECOVERED (%)					88	

^aInjection concentration vs. time record.

^bMean of integrated breakthrough curves from 180-cm ports.

s.d. - standard deviation

Table 5-5. Aromatic hydrocarbon mass balance.

CONTROL CELL											
(mass in grams)											
	Initial Mass	Residual Mass	Flushed Mass				Total Recovered Mass	Mass Loss	Initial Mass Recovered (%)	Initial Mass Flushed (%)	Initial Mass Remaining in Gasoline (%)
			1996	(s.d.)	1997	(s.d.)					
Benzene	640	80	342	(420)	3	(0.8)	425	216	66	54	13
Toluene	4,000	1,460	1,620	(696)	136	(12)	3,216	784	80	44	37
Ethylbenzene	1,760	1,030	385	(41)	35	(1)	1,450	310	82	24	59
m+p - Xylene	3,880	2,330	820	(93)	75	(2)	3,225	655	83	23	60
o-Xylene	1,380	810	339	(39)	30	(2)	1,179	201	85	27	59
135-TMB	570	430	33	(4)	3	(0.1)	466	105	82	6	75
124-TMB	1,760	1,150	111	(15)	11	(0.4)	1,272	488	72	7	65
123-TMB	360	260	32	(4)	3	(0.08)	295	65	82	10	72
Naphthalene	280	240	46	(6)	3	(0.9)	289	-9	103	17	86
Total BTEXTMB	14,630	7,760	3,727	(1,081)	298	(19)	11,785	2,845	81	28	53

NITRATE CELL											
(mass in grams)											
	Initial Mass	Residual Mass	Flushed Mass				Total Recovered Mass	Mass Loss	Initial Mass Recovered (%)	Initial Mass Flushed (%)	Initial Mass Remaining in Gasoline (%)
			1996	(s.d.)	1997	(s.d.)					
Benzene	640	80	540	(431)	4	(0.3)	624	16	98	85	13
Toluene	4,000	1,410	2,166	(937)	136	(9)	3,712	288	93	58	35
Ethylbenzene	1,760	940	403	(30)	36	(0.6)	1,379	381	78	25	53
m+p - Xylene	3,880	2,180	883	(88)	80	(1)	3,143	737	81	25	56
o-Xylene	1,380	750	370	(28)	32	(0.2)	1,152	228	83	29	54
135-TMB	570	410	36	(6)	3	(0.2)	449	121	79	7	72
124-TMB	1,760	1,090	117	(10)	11	(0.6)	1,218	542	69	7	62
123-TMB	360	240	33	(3)	3	(0.2)	276	84	77	10	67
Naphthalene	280	210	49	(5)	4	(1)	263	17	94	19	75
Total BTEXTMB	14,630	7,270	4,598	(1,248)	309	(8)	12,177	2,454	83	34	50

s.d. - standard deviation

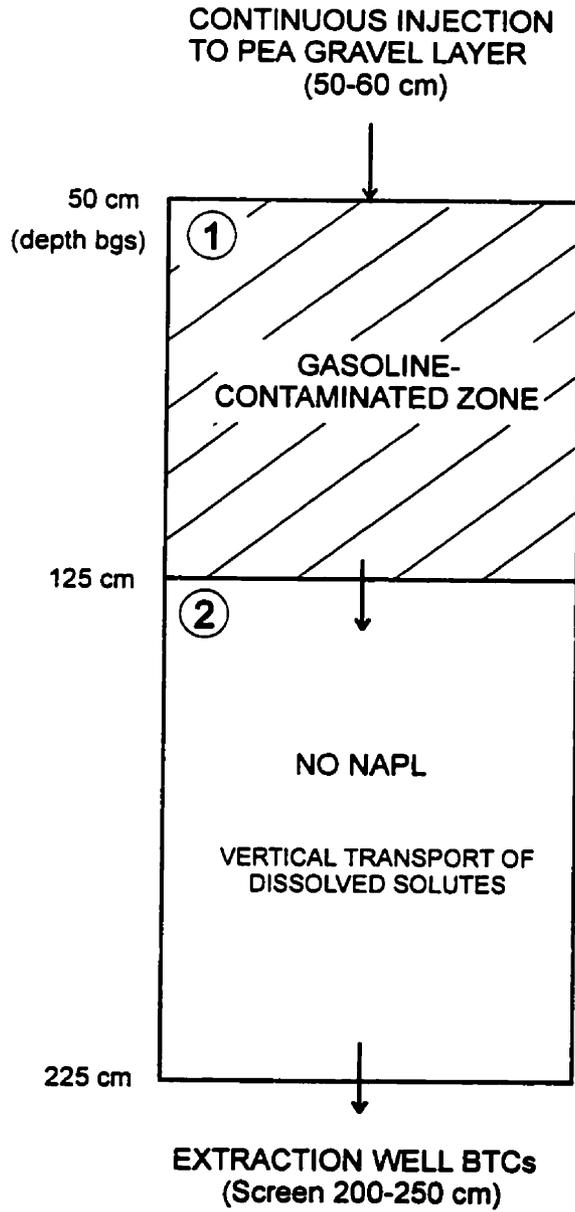
With due consideration of the uncertainty in these field data, the mass balance also provided reasonable qualitative results. As a percentage of initial mass, the gasoline phase in both cells was relatively depleted in the most soluble compounds such as benzene and toluene (despite the high initial mass of toluene in API 91-01), and the majority of relatively insoluble compounds such as naphthalene remained in the residual mass fraction. Similarly, the percentage of initial mass flushed from the cells corresponded fairly well to the effective solubility of the compound. However, there were differences between aqueous concentrations at the end of the experiment and the mass remaining in the residual phase for most aromatic compounds. For example, as shown on Figure 5-9, by the end of the experiment, aqueous concentrations of benzene, toluene, ethylbenzene, total xylenes, and total trimethylbenzenes in the Nitrate Cell had dropped to 1.5%, 39%, 82%, 85%, and 92% of initial gasoline-saturated values measured in the laboratory, respectively, while masses remaining in the gasoline phase declined to 13%, 35%, 53%, 56%, and 65% of initial masses. Assuming equilibrium partitioning (Section 5.3), the changes in aqueous concentration are directly proportional to changes in mole fraction, and should be roughly equal to changes in residual mass. The observed differences may reflect underestimation of the residual mass (Appendix E).

In general, more mass was flushed from the Nitrate Cell than the Control Cell, and residual masses were slightly higher in the Control Cell (Table 5-5). Considering the uncertainty in the analysis, however, it was not possible to conclude that mass losses were greater in one cell relative to the other. This conclusion could only have been made if the difference between cells was large. It is also important to note that this approach does not provide a direct estimate of biotransformation mass loss. The mass loss term, M_{LOSS} , incorporates all mass removal mechanisms, which may include losses from volatilization and cell flooding; although benzene and toluene mass losses were larger in the Control Cell, the differences between cells could conceivably have resulted from abiotic processes, or some other chance event. Moreover, without replicated and properly-interspersed treatments, it would not have been possible to attribute any observed concentration differences to the presence or absence of NO_3^- without other corroborating evidence such as *in situ* patterns of substrate and electron-acceptor utilization or laboratory evidence. The mass balance on the organic compounds was, therefore, most useful in conjunction with the other lines of evidence obtained in this study for the presence or absence of biotransformation.

5.3 Simulation of Aromatic Hydrocarbon Breakthrough Curves

A numerical analysis of the field data was performed to investigate the applicability of simple gasoline dissolution models, to obtain a better general understanding of the effects of stimulating biotransformation within the proximity of a source area, and to provide an additional assessment of the extent of biotransformation in the treatment cells. Simulations of aromatic-hydrocarbon breakthrough curves were performed with a one-dimensional coupled dissolution/solute-transport model. A schematic of the model domain is shown on Figure 5-16. Model results were compared to effluent breakthrough curves obtained from the extraction wells. These wells were used because the breakthrough curves were relatively complete, samples were more representative of bulk concentrations in the cells, and data from the effluent stream corresponded to the longest flowpath in the system. Although the extraction wells cycled on and off during the flushing experiment, with a frequency of approximately 10 cycles per hour, and were susceptible to dilution from uncontaminated water in the underlying aquifer, the effects of these factors on aromatic-hydrocarbon concentrations appeared minimal; in general, concentrations in effluent samples were only slightly lower than piezometer samples from the overlying 180-cm bgs depth interval.

Four major simplifying assumptions were made in constructing the model. First, it was assumed that flow was steady within the treatment cells. This assumption was consistent with the injection procedures (i.e., reasonably constant injection rates and heads under flushing conditions). Second, it was assumed that the flow field was one dimensional. Based on the tracer test data, this assumption was reasonable for the regions of the cells above the extraction wells, but in the vicinity of the extraction wells, the flow field was radial, with significant horizontal flow from the edges of the cells to the centers. The differences in the lengths of flowpaths to the extraction wells led to the relatively large dispersivities calculated from the tracer data (Appendix B). However, the differences in travel times arising from varying flowpath lengths were likely quite small relative to the duration of the field experiment, and the simulated concentration distribution was insensitive to the magnitude of the dispersivity, affecting only initial breakthrough behavior (see below). The use of a simple, one-dimensional model to simulate the extraction-well data was therefore considered acceptable for this application.



VERTICAL EXAGGERATION: 2.5

Figure 5-16. Model domains for coupled dissolution/solute transport simulations.

Third, it was assumed that gasoline dissolution occurred under equilibrium conditions. Under these circumstances dissolution can be characterized by an equilibrium partitioning relationship such as Raoult's Law without an explicit consideration of mass-transfer kinetics. The equilibrium assumption implies that there are no mass-transfer limitations or dilution effects in the NAPL-contaminated region. This assumption was consistent with flow velocities ($v \approx 25$ cm/day, or only 2.5 times the ambient horizontal groundwater velocity in the Borden aquifer), the presence of the sheet-piling walls which minimized bypassing of injected water around the gasoline-contaminated region, and observed aqueous concentrations. Fourth, it was assumed that biotransformation of the aqueous aromatics in the gasoline-contaminated region was negligible. This assumption was consistent with the field and laboratory evidence presented elsewhere in this study. While it is unlikely that there was strict adherence to all of these simplifying assumptions, they provided a reasonable representation of the experimental system, and allowed for independent estimates of all model parameters *a priori*.

As shown in Figure 5-16, a simple two-box model was used to simulate flow and transport in the treatment cells. The upper box, representing the gasoline-contaminated region, was treated as a homogeneous NAPL reservoir. The dissolution process was simulated as a succession of batch equilibrations using a velocity and time step consistent with the actual residence time of the injected fluid in the gasoline-contaminated region. The resulting concentration vs. time records generated for each constituent were then used as the input for the lower box, which represented the one-dimensional flow path for the aqueous-phase contaminants derived from the source area. Thus, for each solute the two boxes were coupled by the time-dependent concentrations, $C_i(t)$, exiting the gasoline-contaminated region. Simulations were performed on a selected group of aromatic hydrocarbons: benzene, toluene, ethylbenzene, *m+p*-xylene, *o*-xylene, and 1,2,4-trimethylbenzene. The simulation approach is described in more detail in the following sections.

Box 1: Dissolution. To simulate the dissolution of a complex, multicomponent organic fluid such as gasoline, for which the molecular composition is not known precisely, a simplified representation of the fluid composition must first be developed. The composition of API 91-01 gasoline is relatively well defined (Appendix A), but pure-phase solubilities are not available for many of the known compounds. Fortunately, because virtually all of these compounds are only sparingly soluble relative to the aromatic hydrocarbons, they can be incorporated into an

unresolved "insoluble" fraction without appreciably affecting the dissolution of the soluble compounds. The gasoline characterization used in this study is shown in Figure 5-17. The 24 known compounds included the most abundant (i.e., > 1% by weight) and soluble C₄ through C₈ alkanes, and the target aromatic hydrocarbons. The size of the group of known compounds was constrained by the need for published pure-phase aqueous solubilities (alkanes, Tissot and Welte (1978); aromatics, Table A-4). Using the weight fractions in Table A-1, known compounds represented 63.3 % by weight of the gasoline. The remaining unidentified fraction of 36.7 % included a large number of low-abundance, relatively-insoluble compounds. This fraction was arbitrarily assigned a "pure-phase" aqueous solubility of 1 mg/L. When varied within a reasonable range (0.5-5 mg/L), aromatic-hydrocarbon dissolution was insensitive to the magnitude of the assigned solubility. Tables A-1 and A-2 indicate that the unidentified fraction consisted of aromatics (10.3 wt. %), alkanes (6.5 wt. %), alkenes (11.8 wt.%), and naphthenes/unknowns (8.1 wt. %).

Aqueous concentrations of the soluble gasoline constituents in equilibrium with the gasoline phase were calculated assuming both ideal and non-ideal behavior in the gasoline phase. As discussed in greater detail in Banerjee (1984), if a hydrophobic organic phase behaves as a non-ideal liquid, and solute interactions in the aqueous phase are small (a reasonable assumption for sparingly-soluble organic compounds), the equilibrium concentration for component i can be described by Equation 5-1

$$C_i^w = \gamma_i^o X_i^o S_i \quad 5-1$$

where the superscripts w and o refer to water and organic phases, respectively, C is the equilibrium aqueous concentration [M/L³], X is the mole fraction [--], S is the pure-phase aqueous solubility [M/L³], and γ is the activity coefficient [--]. If one assumes that the organic phase behaves as an ideal liquid, the activity coefficients for all components in the organic liquid are set to unity, and the equation for Raoult's Law is obtained

$$C_i^w = X_i^o S_i \quad 5-2$$

API 91-01 Gasoline (wt. %)

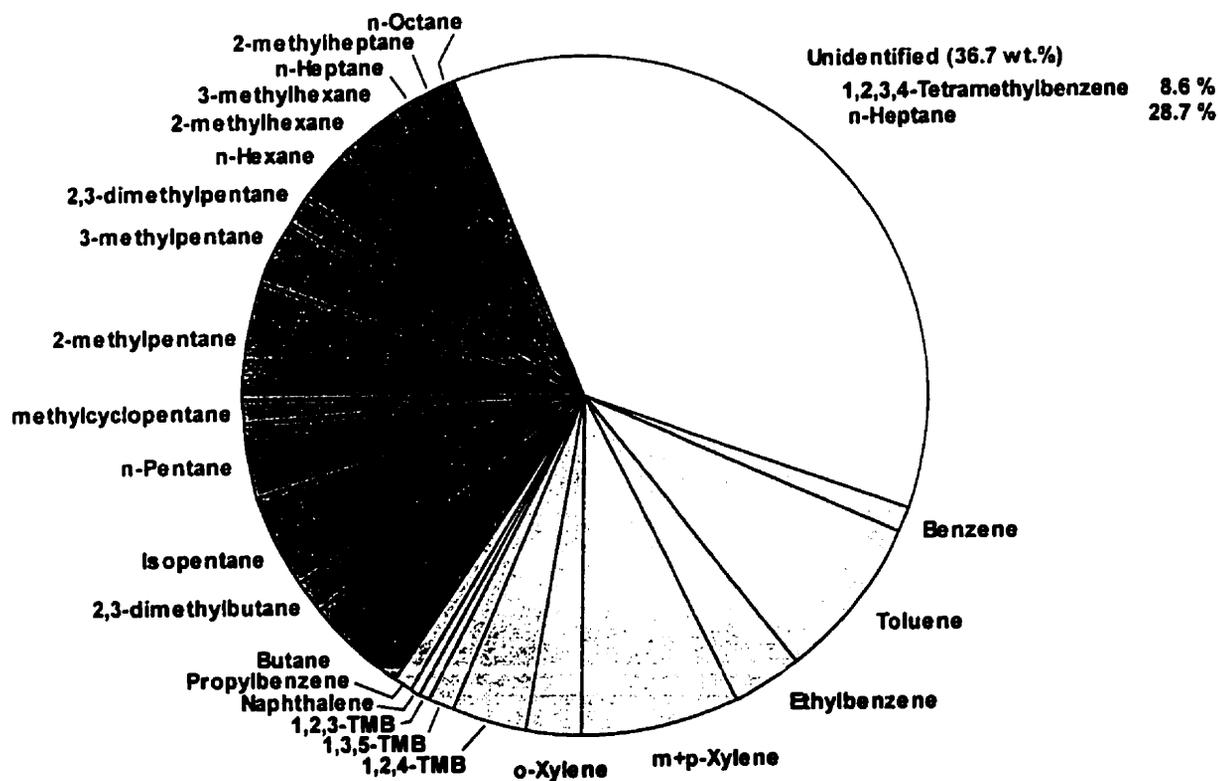


Figure 5-17. Representation of API 91-01 gasoline composition used in dissolution model. Weight fraction data taken from Table A-1

For the API 91-01 gasoline, mole fractions are well-defined, and Raoult's Law provides reasonable estimates (differences within 25%) of measured aqueous aromatic-hydrocarbon concentrations (Appendix A). Concentrations obtained with Raoult's Law were, however, consistently lower than measured concentrations. This systematic difference probably arose from non-ideality in the organic phase, which typically causes the activity coefficients to exceed unity (Mackay et al., 1991; Borden and Kao, 1992).

To improve the agreement between calculated and measured concentrations, activity coefficients were estimated with the UNIFAC model (Fredenslund et al., 1975). This model is based on the group-contribution concept. As such, it treats the liquid as a mixture of the functional groups that constitute the individual compounds. Activity coefficients of each component in the organic mixture are composed of two parts: a combinatorial part and a residual part. The first part reflects non-ideal mixing resulting from the size and interaction surface areas of individual functional groups, and the second from energetic interactions between these functional groups (Fredenslund et al., 1975). One limitation of the method is that, as a group contribution model, distinctions between isomers are not possible. To calculate activity coefficients with UNIFAC, mole fractions for every component in the mixture are required. In this study, it was necessary to define the unidentified fraction of the gasoline in terms of representative compounds. Because this fraction had both aromatic and aliphatic characteristics, it was represented by 1,2,3,4-tetramethylbenzene (8.6 wt. %) and n-heptane (28.8 wt. %) in the model. These compounds were selected because their molecular weights were appropriate; with the weight percents listed above, the molecular weight for the simulated gasoline was very close to the actual weight of 94 g/mole.

Activity coefficients calculated with the UNIFAC model (10°C) were generally slightly greater than unity (Table 5-6). A sensitivity analysis indicated that the model was not sensitive to the specific aromatic or aliphatic compound used to define the unidentified fraction (e.g., n-heptane vs. n-hexane). Similarly, it was not sensitive to the presence or absence of a naphthene in the aliphatic fraction. It was, however, sensitive to the presence of an aromatic compound; when the unidentified fraction was defined as entirely aliphatic in character, activity coefficients for the aromatic hydrocarbons were larger. In the most rigorous analysis, activity coefficients would be continuously updated as the composition of the organic fluid changed during dissolution. A sensitivity analysis on the API 91-01 gasoline indicated, however, that the error introduced by

Table 5-6. Activity coefficients for constituents of fresh API 91-01 gasoline at 10°C calculated with the UNIFAC model. The unidentified fraction of the gasoline (X=0.33) was represented by n-heptane (X=0.27) and 1,2,3,4-tetramethylbenzene (X=0.06).

Compound	Mole Fraction (X)	Activity Coefficient (γ)
Benzene	0.0147	1.18
Toluene	0.0784	1.23
Ethylbenzene	0.0298	1.17
m+p-Xylene	0.0659	1.19
o-Xylene	0.0234	1.19
1,2,4-Trimethylbenzene	0.0264	1.10
1,3,5-Trimethylbenzene	0.0086	1.10
1,2,3-Trimethylbenzene	0.0053	1.10
Naphthalene	0.0039	1.72
Propylbenzene	0.0059	1.12
Butane	0.0789	0.99
2,3-Dimethylbutane	0.0180	1.053
Isopentane	0.0588	1.038
n-Pentane	0.0470	1.038
Methylcyclopentane	0.0124	1.030
2-Methylpentane	0.0602	1.054
3-Methylpentane	0.0340	1.054
2,3-Dimethylpentane	0.0122	1.067
n-Hexane	0.0289	1.055
2-Methylhexane	0.0153	1.049
3-Methylhexane	0.0159	1.049
n-Heptane	0.0122	1.050
2-Methylheptane	0.0070	1.028
n-Octane	0.0054	1.028
1,2,3,4-Tetramethylbenzene	0.0601	0.98

using the initial activity coefficients over a 300-day simulation was minimal (<5%). The initial activity coefficients listed in Table 5-6 were therefore used in all subsequent simulations. A comparison between calculated BTEXTMB concentrations assuming ideality ($\gamma_i = 1$; Raoult's Law) and non-ideality ($\gamma_i \neq 1$; UNIFAC) is shown in Figure 5-18. With the assumption of non-ideal behavior in the gasoline phase, calculated aqueous concentrations were closer to observed, but remained lower for most of the aromatic compounds.

Following the gasoline characterization, a simple advective model was used to simulate dissolution using the representation of the API 91-01 gasoline shown in Figure 5-17. In simulating dissolution with a 1-box model, the assumptions were made that gasoline-water equilibration was instantaneous and spatially-uniform throughout the gasoline-contaminated region as dissolution progressed, and that there was perfect contact between the phases. To perform the simulations, the total moles of gasoline constituents in the cell were first normalized to a unit area. Equation 5-1 was then used to calculate aqueous concentrations in equilibrium with fresh gasoline. For each constituent, the model then calculated the aqueous mass removed during the initial time step. Mass removal of constituent *i* from the gasoline-contaminated region was calculated from the advective flux of gasoline-saturated water, which was assumed to be constant over the time step

$$M_i = \bar{v}C_i t \quad 5-3$$

where *M* is the mass removed per unit area [M], \bar{v} is the average linear groundwater velocity [L/T], *C* is the concentration in gasoline-saturated water [M/L³], and *t* is the length of the time step. The groundwater velocity was calculated from Q/nA , where *Q* is the mean injection rate in each cell [L³/T], *A* is the cell cross-sectional area [L²], and *n* the assumed porosity. The effects of sorption were ignored within the gasoline-contaminated region. At the end of the time step, mass removal was used to update the gasoline composition and the corresponding mole fractions, and then to calculate new aqueous concentrations using Equation 5-1. Aqueous concentrations in equilibrium with the new gasoline composition were then used to calculate mass removal for the following time step using Equation 5-3. These calculations were repeated for all subsequent time steps. Thus, the model effectively performed a series of batch equilibrations under continuous flow conditions to estimate NAPL dissolution, and the corresponding time-dependent concentrations exiting the gasoline-contaminated region.

Concentration in Water Equilibrated With API 91-01

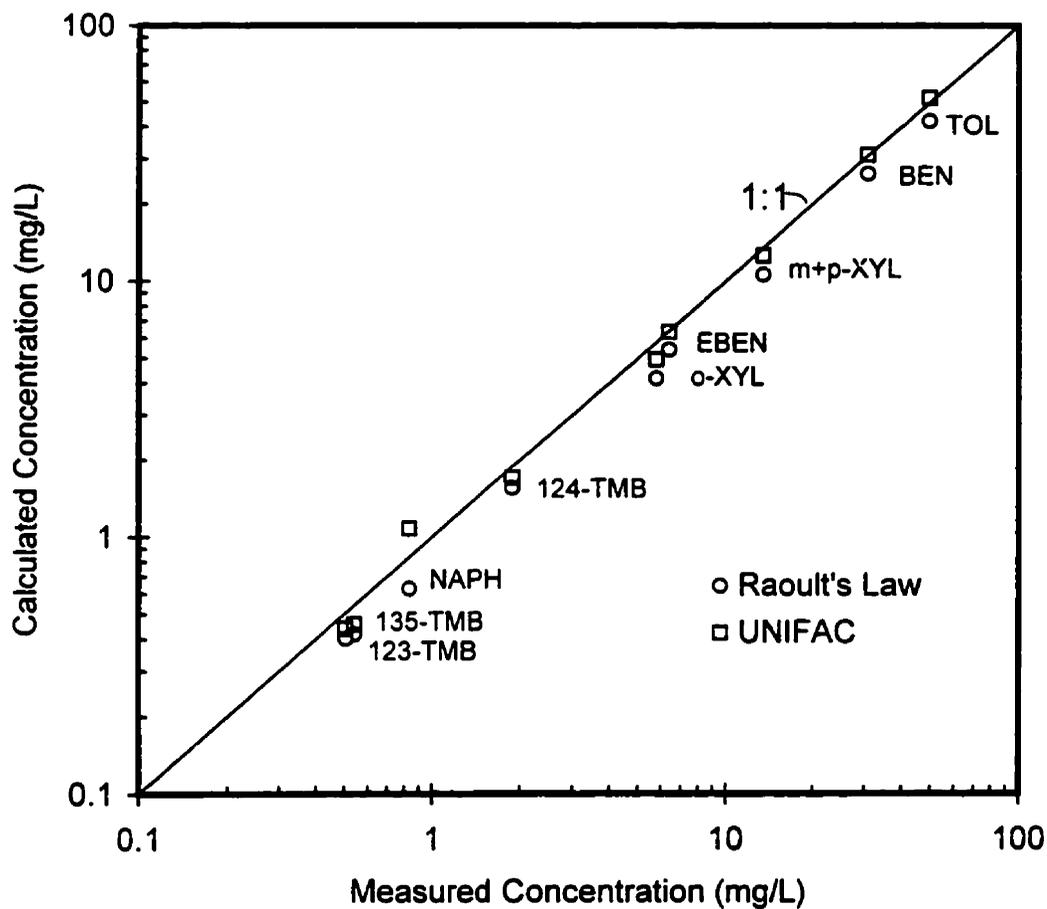


Figure 5-18. Calculated vs. measured BTEXTMB concentrations in gasoline-saturated water. Measured concentrations obtained from equilibration of water with fresh API 91-01 gasoline as described in Appendix A.

As an example of the model output, concentration trends for selected constituents in the Nitrate Cell are shown in Figure 5-19. The rapid depletion of the soluble constituents such as benzene and toluene is clearly evident. In the field, the residence time of injected water within the gasoline-contaminated region was roughly 3 days (75 cm flow path at 25 cm/day groundwater velocity). Accordingly, a three-day time step was used in the simulations. Sensitivity analyses showed, however, that aqueous concentrations, particularly for the less soluble constituents, were insensitive to the length of the time step. For example, after 200 days, simulated toluene concentrations were 21.6 mg/L and 21.5 mg/L for time steps of two and five days, respectively. This dissolution model is relatively sensitive to the injection rate because under equilibrium-partitioning conditions the mass removed during a given time step is directly proportional to the magnitude of the rate. As a consequence, concentrations decline more rapidly in response to higher injection rates. Fortunately, the values of the injection rates, and hence vertical flow velocities, were well constrained by periodic measurements made during the flushing experiment (Figure 3-8). To avoid using velocity as a curve-fitting parameter, all simulations presented below were performed with the measured mean injection rates of 251 ml/min and 237 ml/min for the Nitrate and Control Cells, respectively. Using a cell cross-sectional area of 4 m² and a porosity of 0.33, these rates correspond to average linear groundwater velocities of 27.3 cm/day and 25.8 cm/day.

Simulations with 70 liters of API 91-01 gasoline assume that the entire volume of gasoline released into the cells was in contact with the injected water. Clearly, however, the treatment of the gasoline-contaminated zone as a homogeneous region is an oversimplification of field conditions. For example, as flushing proceeded depletion of the relatively-soluble compounds was much more rapid at some piezometer locations relative to others (Figure 5-11 and 5-12), which probably resulted from spatial variability in residual gasoline saturation. The heterogeneity in gasoline distribution is also clearly shown in the vertical profiles developed from the core-extract samples (Figures 5-14 and 5-15). Although the tracer test indicated that injected water was fairly well distributed in both cells (Appendix B), it is reasonable to anticipate that some fraction of the emplaced source mass was not in direct contact with the injected fluid. If some of the gasoline phase was bypassed by the injected fluid, a 1-box dissolution model based on uniform dissolution of the total released (larger) volume would overestimate effluent concentrations, particularly for the soluble constituents that become depleted over the time periods under consideration here.

Concentrations in Gasoline-Saturated Groundwater
 $v = 27.3$ cm/day, Non-Ideal (UNIFAC)

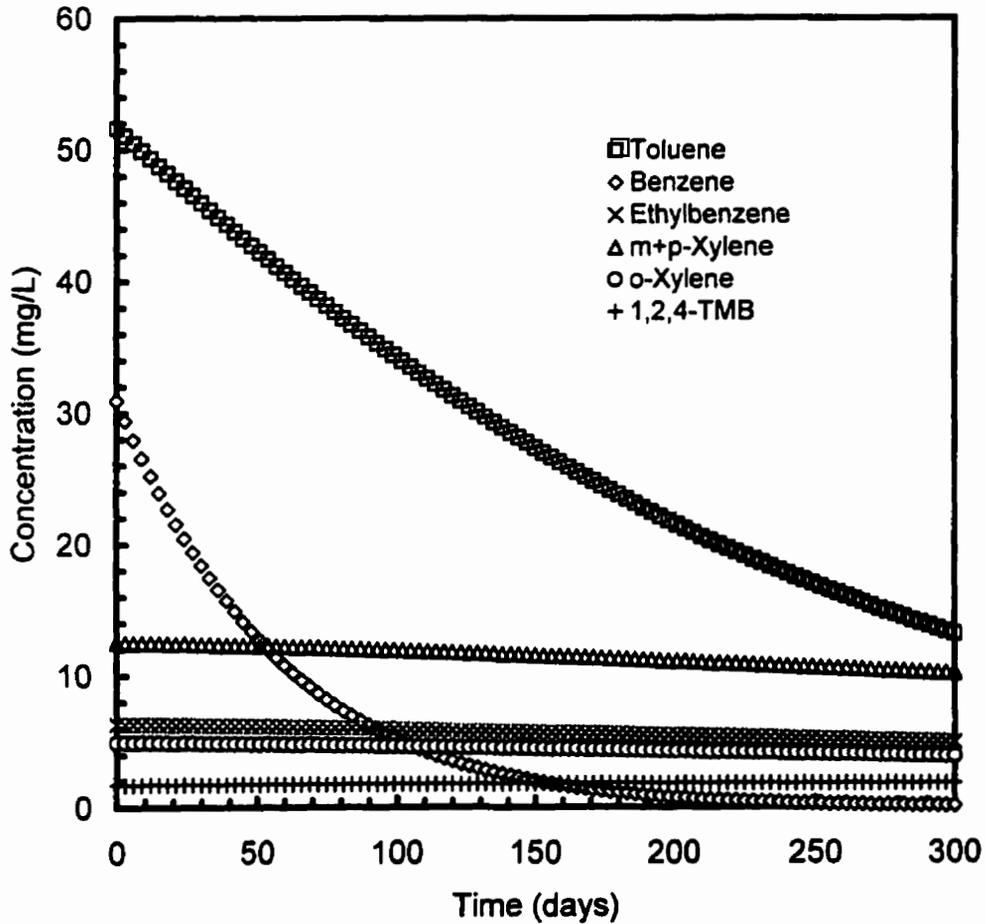


Figure 5-19. Example of dissolution model output for 70-L volume of API 91-01 gasoline. Symbols represent the calculated aqueous concentration of a constituent in equilibrium with the gasoline phase during a three-day time-step.

To further evaluate the assumption of uniform dissolution of the total released volume in the gasoline-contaminated region, the ratio mass estimation (RME) approach developed by Devlin (In Submission) was also applied to the field data. This method allows for an estimation of the initial mass of NAPL using aqueous concentration ratios. There are two main advantages of using concentration ratios. First, because dilution affects all aqueous constituents to the same degree, a model based on concentration ratios will be insensitive to dilution effects. Second, the relative aqueous concentrations of NAPL constituents are independent of the composition of the unknown fraction of the NAPL. This approach can therefore provide estimates of initial NAPL mass with relatively little knowledge of NAPL characteristics.

The theoretical basis for the approach is described in Devlin (In Submission), and will not be repeated in detail here. In brief, the method is based on a similar set of initial assumptions as the dissolution model described above, i.e., advective transport of water through the NAPL with equilibrium partitioning between the two phases. In this study, activity coefficients estimated with the UNIFAC model were incorporated into the analysis, while Devlin (In Submission) used Raoult's Law. The equation describing aqueous mass removal from the NAPL is equivalent to Equation 5-3, except that the equilibrium concentration of the solute is expressed explicitly in terms of Equation 5-1, and the equation is expressed in differential form

$$\frac{dM_i}{dt} = X_i S_i \gamma_i Q \quad 5-4$$

where Q is the volumetric flow rate through the NAPL [L^3/T] (taken here as equivalent to the mean injection rates), and all other parameters are as defined previously. If the mole fraction is expressed in terms of a constituent's mass, molecular weight, and the total moles in the NAPL mixture, Equation 5-4 can be solved, and then expressed as a ratio to obtain the following RME equation for aqueous constituents i and j

$$\ln\left(\frac{C_i}{C_j}\right) = \ln A - \frac{Q B}{K} t \quad 5-5$$

where,

$$A = \frac{M_o S_i \gamma_i W_j}{M_o S_j \gamma_j W_i} \quad 5-6$$

and,

$$B = \frac{S_i \gamma_i}{W_i} - \frac{S_j \gamma_j}{W_j} \quad 5-7$$

The parameter K is the total moles of constituents in the NAPL, W is the molecular weight [M/mole], M_o is the initial mass of the constituent [M], and the other parameters are as defined previously. Equation 5-5 indicates that the concentration ratio vs. time relationship will be linear on a semi-log plot. Both A and B consist only of constants, and B can be calculated *a priori* from known values. The quantity K can then be obtained from the slope of Equation 5-5, and the NAPL mass can be calculated from the molecular weight of the organic fluid.

In this study, the initial gasoline mass in each cell was estimated from extraction-well data using concentration ratios of three solute pairs: Toluene/Benzene, Ethylbenzene/Benzene, and Ethylbenzene/Toluene. Extraction-well concentration data (Figure 5-8) plotted as $\ln(C_i / C_j)$ vs. time are shown on Figures 5-20 and 5-21 for the Nitrate and Control Cells, respectively. The relevant compound properties, parameter values, and resulting mass estimates are summarized in Table 5-7. For both cells, all three solute pairs produced similar initial gasoline mass estimates. Gasoline masses were calculated from the total number of moles of gasoline using the molecular weight of API 91-01 of 94 g/mole. Mean initial masses were 40.1 kg and 34.7 kg in the Nitrate and Control Cells, respectively. Using the measured gasoline density of 0.747 g/cm³ these masses represent volumes of 54 L (Nitrate Cell) and 46 L (Control Cell), or 77% and 66% of the total 70-L volumes released into the cells.

This analysis suggested that the volumes of gasoline in contact with injected water were somewhat less than the total released volumes. This may reflect heterogeneities in the treatment

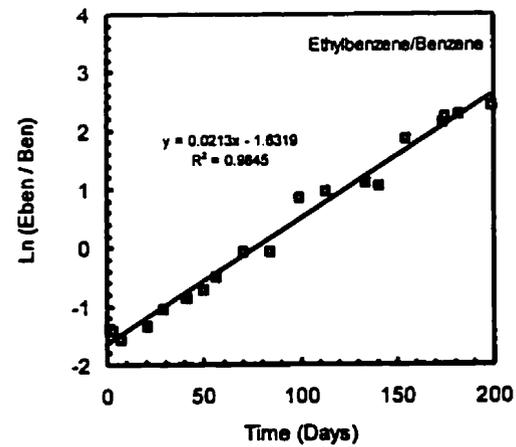
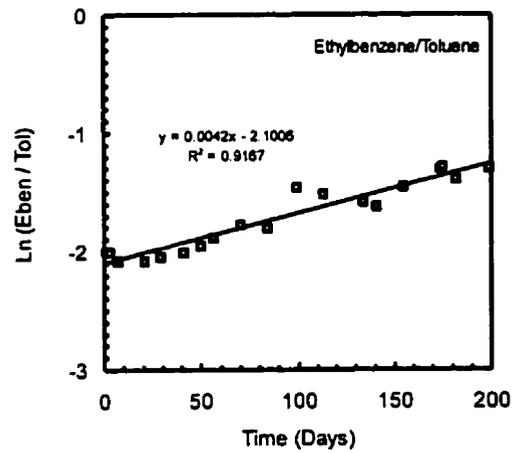
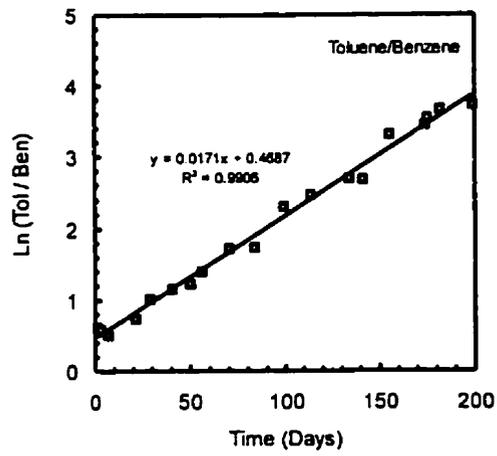


Figure 5-20. Concentration ratios in samples collected from the extraction well in the Nitrate Cell.

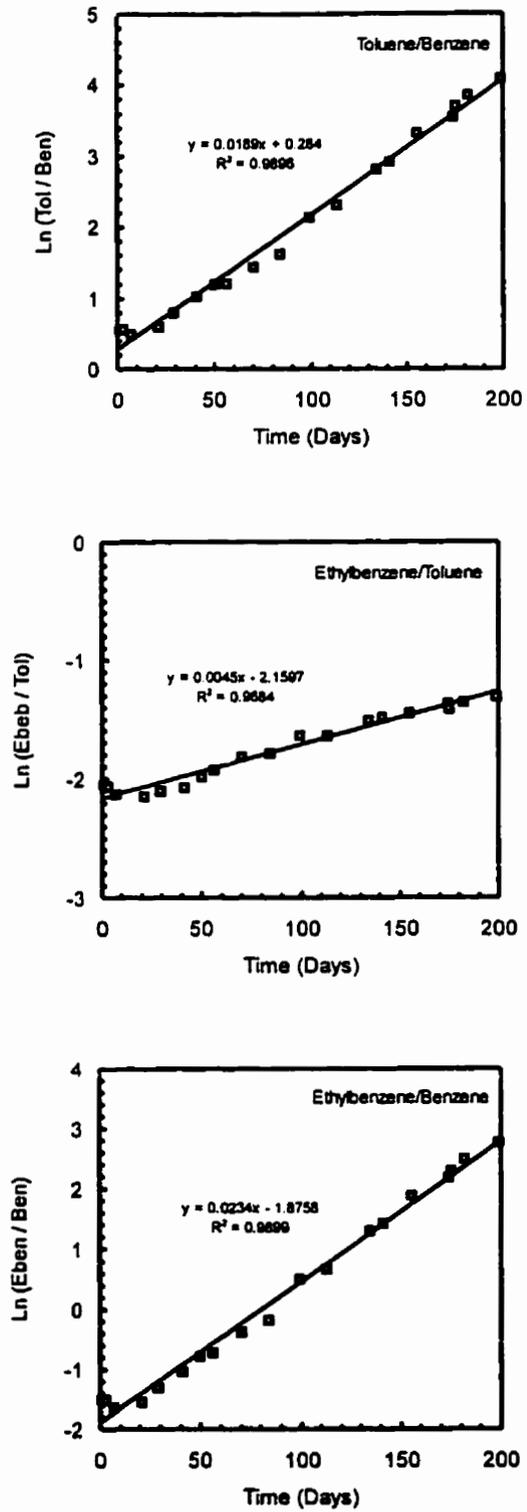


Figure 5-21. Concentration ratios in samples collected from the extraction well in the Control Cell.

Table 5-7. Gasoline mass estimates from RME analysis.

Parameter	Nitrate Cell			Control Cell		
	Tol/Ben	Eben/Tol	Eben/Ben	Tol/Ben	Eben/Tol	Eben/Ben
Mean Injection Rate (L/day)	360	360	360	341	341	341
Initial NAPL Mass (kg)	54.3	54.3	54.3	54.3	54.3	54.3
Initial Mass Ratio	6.3	0.44	2.8	6.3	0.44	2.8
B ¹ (moles/L)	-0.0198	-0.00515	-0.0249	-0.0198	-0.00515	-0.0249
slope (day ⁻¹)	0.0171	0.0042	0.0213	0.0189	0.0045	0.0234
ln A	0.4687	-2.1006	-1.6319	0.284	-2.1597	-1.8758
K (moles)	416	441	421	356	390	362
Calculated Initial Mass Ratio	6.0	0.29	2.6	5.0	0.27	2.1
Calculated NAPL Mass (kg)	39.1	41.5	39.6	33.4	36.7	34.1

¹Compound Properties:

Toluene: S=535 mg/L; γ =1.23; W=92.13 g/mole

Ethylbenzene: S=181 mg/L; γ =1.17; W=106.2 g/mole

Benzene: S=1780 mg/L; γ =1.18; W=78.11 g/mole

cells, including spatial differences in gasoline saturation and aquifer permeability within the flow field, and the presence of gasoline above the active flow system. On the other hand, considering the uncertainty associated with some of the parameters involved in the calculations these initial gasoline volumes were reasonably close to 70 liters. Apparently, forcing flow through a region that contained a relatively-uniform distribution of NAPL from a recent spill produced conditions in which the gasoline and aqueous phases were in good contact. In the simulations performed below, effluent breakthrough curves were obtained using both 70 liters (as a baseline simulation) and the smaller gasoline volumes estimated with the RME approach.

The RME analysis provided additional useful information. The strong linearity observed for all solute pairs indicated that the underlying assumptions of the method were not violated. In particular the results suggested that the equilibrium assumption was valid, that the total number of moles of gasoline remained constant over 200 days of injection, and that reactions (i.e., transformations and sorption) had not substantially altered solute concentrations along the flowpath. In addition, as noted by Devlin (In Submission), when a dissolution front progresses through a NAPL-contaminated region, concentrations exiting this region can remain constant for an extended period of time, leading to a very low slope on a concentration-ratio vs. time semi-log plot, and excessively high NAPL mass estimates with an RME analysis. While there was some evidence from concentration profiles of progressive vertical depletion of the aromatics (Figure 5-10), pronounced concentration trends indicative of dissolution fronts were not observed in the data collected in this study (Figures 5-8, 5-20 and 5-21). Thus, the linear relationships and reasonable mass estimates obtained from the RME analysis provided support for the use of a simple 1-box dissolution model (that necessarily assumes spatially-uniform dissolution) within the gasoline-contaminated region.

Box 2: Flow and Transport of Aromatic Hydrocarbons. Migration of the aqueous aromatic hydrocarbons below the gasoline-contaminated region was simulated with a one-dimensional analytical model originally developed to simulate tritium distribution in groundwater (Egboka et al., 1983; Robertson and Cherry, 1989). The model was used to investigate tritium distributions along horizontal or vertical one-dimensional flowpaths. A method based upon superposition of solutions was used to represent the variable tritium content in recharging precipitation. In this study, the analytical solution was modified to incorporate adsorption. In

addition, the solution method was modified to calculate a breakthrough curve rather than a one-dimensional concentration profile along a flowpath.

When adsorption can be described by a linear isotherm, the one-dimensional advection-dispersion equation for a biotransformable solute in a saturated porous medium is

$$\frac{\partial C}{\partial t} = \frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} - \frac{\lambda}{R} C \quad 5-8$$

where D_x is the dispersion coefficient in the direction of flow [L^2/T], λ is the first-order rate constant for biotransformation [$1/T$], R is the retardation factor [--], and all other parameters are as described above. In describing adsorption with a retardation factor, it is assumed that sorption is instantaneous, reversible, independent of contaminant concentrations, and uniform throughout the volume of interest. In this formulation, there is no biotransformation of the sorbed phase. The dispersion coefficient was defined here as

$$D_x = \alpha_L \bar{v} + D^* \quad 5-9$$

where α_L is the longitudinal dispersivity [L] and D^* is the effective diffusion coefficient in a porous medium [L^2/T]. The effective diffusion coefficient was assumed to be zero in the simulations performed in this study. For the initial and boundary conditions

$$C = C_0, \quad x = 0$$

$$\frac{\partial C}{\partial x} = 0, \quad x = \infty$$

$$C = 0, \quad t = 0$$

where C_0 is the source concentration, the solution, as given by Robertson and Cherry (1989), is

$$C(x,t) = \frac{1}{2} C_0 \left[\exp\left(\frac{\bar{v}x}{2D_x} - \frac{x}{\sqrt{D_x}} \sqrt{\frac{\bar{v}^2}{4D_x} + \lambda}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{D_x t}} - \sqrt{\left(\frac{\bar{v}^2}{4D_x} + \lambda\right) t}\right) \right. \\ \left. + \exp\left(\frac{\bar{v}x}{2D_x} + \frac{x}{\sqrt{D_x}} \sqrt{\frac{\bar{v}^2}{4D_x} + \lambda}\right) \operatorname{erfc}\left(\frac{x}{2\sqrt{D_x t}} + \sqrt{\left(\frac{\bar{v}^2}{4D_x} + \lambda\right) t}\right) \right] \quad 5-10$$

For sorbing compounds, \bar{v} is replaced by \bar{v}/R , D_x by D_x/R , and λ by λ/R (Bear, 1979). To represent the temporal variability of solute concentrations in groundwater entering the model domain, the superposition of solutions technique described by Egboka et al. (1983) and Robertson and Cherry (1989) was used. In this study, the 300-day concentration profiles from the dissolution model (e.g., Figure 5-19) were treated as discrete step functions, with a single concentration value for each three-day time step. The solution was validated by comparison with output from SALTFLOW, a flow and mass-transport finite-element model that can accommodate a variable input concentration.

Sensitivity analyses on the retardation factor, dispersivity, and flowpath length were performed prior to simulating the field data. The baseline parameter values for these simulations were $R=1.5$, $\alpha_L = 20$ cm, $\bar{v} = 27.3$ cm/day, $L=100$ cm, and $\lambda = 0$ (no biotransformation). Toluene source concentrations were calculated with the dissolution model assuming non-ideality in the gasoline phase and a 70-L volume. All sensitivity analyses were performed with a four-day time step, and results were plotted with the measured toluene breakthrough curve from the Nitrate Cell.

The length of the flowpath, L , could not be defined precisely because the thickness of the gasoline-contaminated region was variable, being thicker in the centers of the cells near the gasoline injection wells, and because the effluent data were collected from extraction wells with 50-cm screens. Simulation results were, however, insensitive to the length of the flowpath when the value was varied over a physically-realistic range of 75 to 125 cm (not shown). In the schematic of the model domain (Figure 5-16), the length of the flowpath is given as 100 cm, which

represents the distance to the midpoint of the extraction well screen using a rough average of 75 cm for the vertical thickness of the gasoline-contaminated region. This length was used in all subsequent simulations.

A sensitivity analysis with $\alpha_L=1, 5,$ and 50 cm indicated that the shape of the simulated concentration distribution was somewhat sensitive to the dispersivity value during early time, but much less so after the initial arrival of the solute (not shown). Because of the lack of sensitivity and because a close fit to the early-time data was relatively unimportant, this parameter was not used to calibrate the model. Simulations in both treatment cells were performed with dispersivities obtained from the tracer test ($\alpha_L=13.4$ cm, Control Cell; $\alpha_L= 5.3$, Nitrate Cell).

As expected, a sensitivity analysis on the retardation factor showed that the solute migration rate decreased as the retardation factor increased from $R=1$ (no sorption) to $R=4$ (Figure 5-22). However, the length of the flowpath was short, and differences in the simulated solute distribution were fairly small after the arrival of the solute front. For the simulations shown below, retardation factors were estimated *a priori* for each solute using well-known estimation procedures based on the organic carbon content of the aquifer sediment. For a given compound, the distribution coefficient, K_d , was first approximated from the relationship $K_d = f_{oc}K_{oc}$ where f_{oc} is the average weight fraction of organic carbon in the Borden aquifer (0.0002), and K_{oc} is the organic-carbon-based partition coefficient for each solute. In this study the K_{oc} values were estimated from a published correlation with the octanol-water partition coefficient, K_{ow} : $\log K_{oc} = 0.937 \log K_{ow} - 0.006$ (Lyman et al., 1982). Values for K_{ow} were obtained from the published literature. Retardation factors were then calculated using the well-known expression $R = 1 + (\rho_b/n)K_d$ where ρ_b is the dry bulk density (1.82 g/cm^3) and n is the porosity (0.33). Uncertainties in the values for bulk density and porosity are typically very small relative to the uncertainty in K_d values (Patrick et al., 1985). The following retardation factors were obtained from this estimation method: benzene, 1.1; toluene, 1.4; ethylbenzene, 2.2; *m+p*-xylene, 2.1; *o*-xylene, 1.9; and 1,2,4-trimethylbenzene, 3.8.

The calculated retardation factors for BTX were in good agreement with values obtained from laboratory batch tests (Patrick et al., 1985). Nonetheless, these retardation factors are considered only rough approximations of the extent of sorption because at least two of the

Retardation Factor

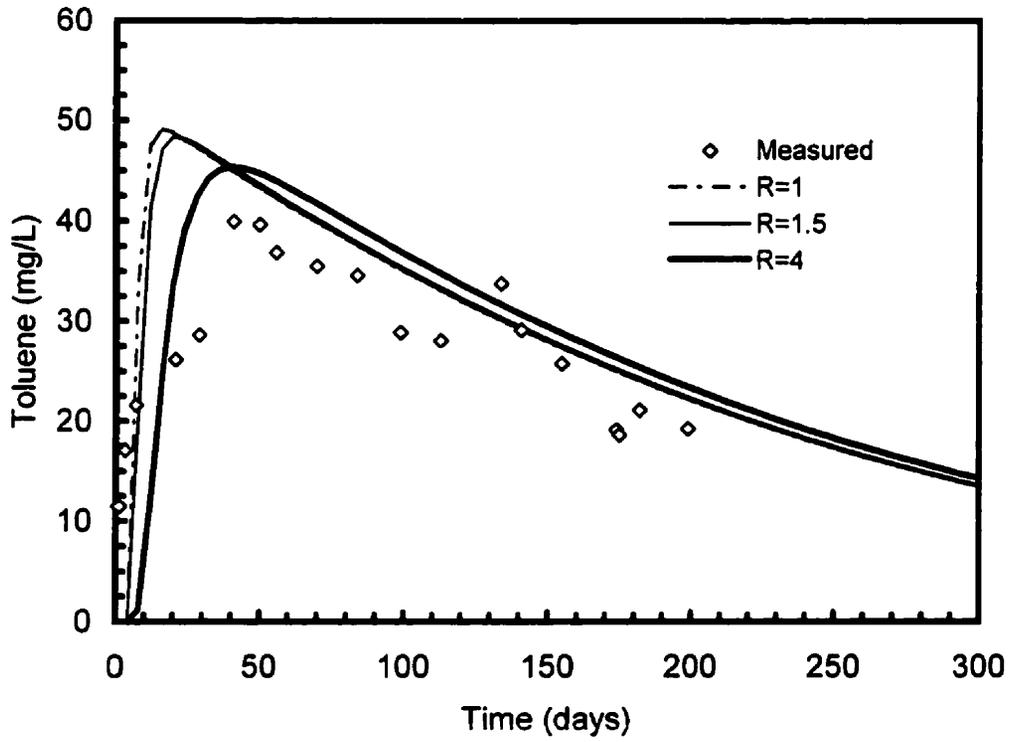


Figure 5-22. Retardation coefficient sensitivity analysis.

underlying assumptions may have been violated. First, sorption may not have been spatially uniform within the treatment cells. Retardation factors calculated with the average f_{oc} of the Borden aquifer may not have been representative of sorption within certain regions of the cells, particularly if peat and associated organic-rich sediments were present in substantial quantities near the base of the active flow system. As discussed previously, efforts were made to install the extraction wells above the peat layer, but the distribution of the peat was patchy and its presence at higher elevations cannot be precluded. Second, there is laboratory evidence of mild non-linearity in sorption isotherms in this aquifer (Unpublished Data). Departures from linearity suggested that sorption would be weaker at high solute concentrations. Consequently, a single retardation factor may not have been representative of sorption over the wide range of solute concentrations and organic-carbon levels in the treatment cells. However, these complexities were not addressed further because reasonably good fits to the early-time data were obtained with the calculated retardation factors given above, and close fits were not critical for simulating trends in solute distribution over a 300-day time period.

Simulated and observed extraction-well breakthrough curves for the selected aromatic hydrocarbons are shown in Figures 5-23 and 5-24. The values for the model parameters were as follows: $L=100$ cm; $\alpha_L=5.3$ cm (Nitrate Cell); $\alpha_L=13.4$ cm (Control Cell); $\bar{v}=27.3$ cm/day (Nitrate Cell); $\bar{v}=25.8$ cm/day (Control Cell); $R=1.1$ (benzene), 1.5 (toluene), 2.0 (ethylbenzene, *m+p*-xylene, *o*-xylene), 4.0 (1,2,4-trimethylbenzene). Biotransformation was assumed to be negligible in the experimental system ($\lambda=0$). Figures 5-23 and 5-24 show that the model was able to capture the general trends in solute distribution over a 200-day flushing period. Effluent concentrations of the most soluble compounds (benzene and toluene) declined noticeably during this period, while concentrations of the less soluble compounds remained steady. The smaller gasoline volumes obtained from the RME analysis improved the fits for benzene and toluene. In contrast, the less-soluble constituents were relatively insensitive to the volume of gasoline over the time period simulated here. In general, consistent with the batch equilibration experiments where measured concentrations were greater than calculated (Figure 5-18), the model slightly underpredicted the field data for most compounds. This occurred despite processes such as dilution, biotransformation, and volatilization that could potentially lower concentrations in the field.

Nitrate Cell

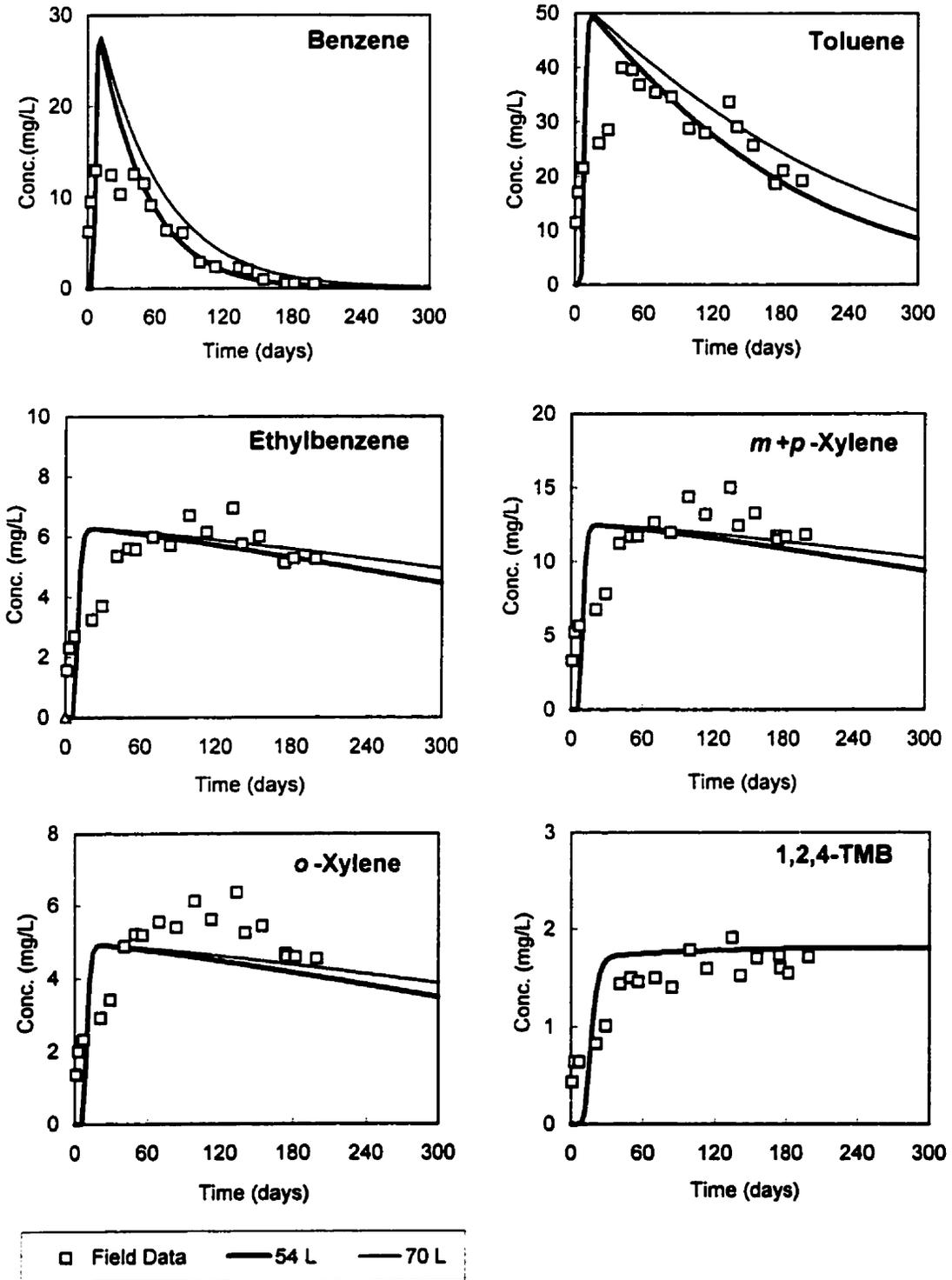


Figure 5-23. Simulated and measured effluent breakthrough curves for selected constituents in the Nitrate Cell.

Control Cell

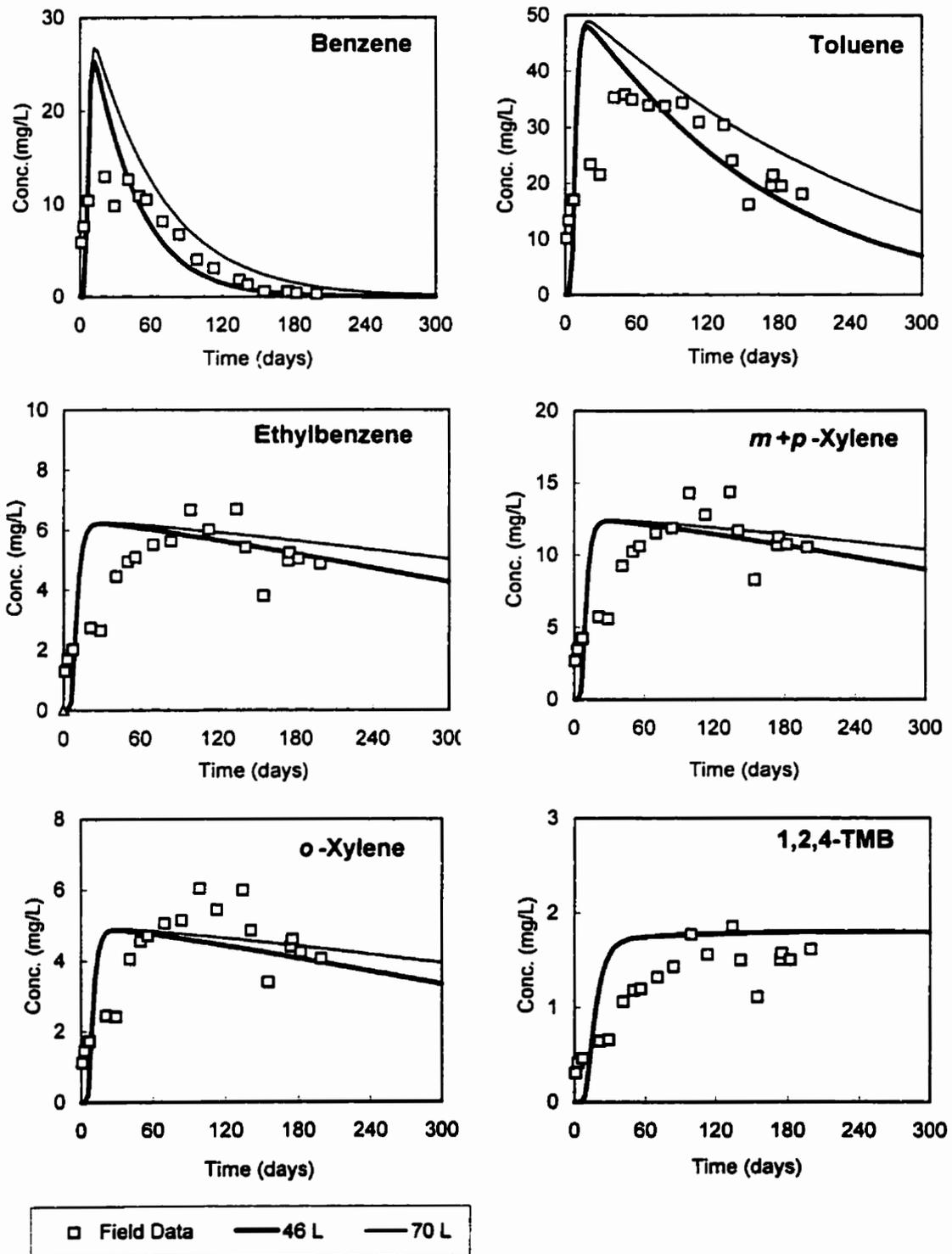


Figure 5-24. Simulated and measured effluent breakthrough curves for selected constituents in the Control Cell.

In general, fits to the early-time data were relatively poor because observed breakthrough of maximum concentrations occurred later than model predictions. These differences may have been related to migration velocities (i.e., sorption), the effects of dilution on the effluent concentrations, variability from early operational problems (Section 3.4.3), or some combination of these factors. As discussed previously, however, a close fit to the early-time data was not critical for comparing simulated and measured concentrations over the entire 200-day flushing period. Moreover, the sensitivity analyses performed as part of this analysis showed that transport parameters such as the dispersivity, retardation factor, and flowpath length were relatively unimportant, having only minor effects on the position and shape of the initial arrival of the contaminant front. In retrospect, therefore, a simpler model based solely on the measured flux of water through the gasoline-contaminated region (i.e., the 1-box dissolution model) would have been adequate in this application for comparing observed concentrations near the source area with calculated concentrations in equilibrium with gasoline-saturated water as dissolution proceeded.

Nonetheless, the simple 2-box analysis performed here proved to be a useful tool for evaluating the field data; specifically, it provided additional insight into the relative effects of transport, reaction, and dissolution on concentration distributions exiting the treatment cells. Most importantly for evaluating the effects of electron-acceptor replenishment, the simulations provided additional evidence for a lack of substantial biotransformation within the treatment cells; the simulations clearly indicated that the observed contaminant mass fluxes from the source area were not decreased relative to the fluxes predicted to result from abiotic gasoline dissolution. A reaction term (i.e., biotransformation) was not required to obtain good agreement with the field data. The RME analysis also suggested strongly that biotransformation losses were minor in the treatment cells. The results of these analyses were therefore consistent with the experimental evidence presented elsewhere in this study.

5.4 Discussion and Conclusions

Despite the uncertainty associated with the low-concentration O₂ data, Figure 5-1 clearly shows rapid depletion of the majority of the O₂ injected into the treatment cells. After about 15 days in the Nitrate Cell and 60 days in the Control Cell, groundwater collected from the pea-gravel layer (60-cm bgs sampling ports) was typically at the threshold O₂ concentration; depletion

therefore occurred within hours of injection. Downward migration of dissolved O_2 probably did not exceed ca. 10 cm. The same pattern was observed when the injection dissolved- O_2 concentration was increased to approximately 5 mg/L during the 24-day flushing period the following spring. These results are consistent with the rapid utilization of dissolved O_2 in laboratory microcosms that contained contaminated aquifer material. In the laboratory, aromatic-hydrocarbon losses were observed under aerobic conditions. In the field, however, losses of aromatic hydrocarbons were not evident. Microaerophilic O_2 may also have been consumed in reactions with other gasoline hydrocarbons or inorganic species, but the occurrence and extent of these reactions could not be clearly established with the data collected here.

In contrast to rapid dissolved- O_2 utilization, NO_3^- uptake was relatively low. Most of the NO_3^- depletion appeared to occur initially in the presence of dissolved O_2 , possibly to satisfy an assimilatory nitrogen requirement, as observed in other studies (Bazyliniski and Blakemore, 1983). Previous studies have also shown that the activity of microorganisms in the Borden aquifer is nitrogen-limited under aerobic conditions (Barbaro et al., 1994). Additional NO_3^- utilization probably occurred under O_2 -depleted conditions, but rates were too low to observe much depletion during the nine-day flushing residence time. Thus, a large denitrifying population capable of rapid NO_3^- uptake did not develop over the time period investigated in this study in response to exposure to abundant substrate and NO_3^- . The NO_3^- concentration profile obtained under static conditions at the 180-cm depth interval showed that about five months were required to fully deplete the added NO_3^- (i.e., a zero-order rate of 0.67 mg NO_3^- /L/d). Although NO_3^- utilization was observed, additional data collected during the static period suggested that the aromatic hydrocarbons were not the preferred substrates under anaerobic, denitrifying conditions in this highly-contaminated, multiple-substrate system. This conclusion is consistent with the laboratory experiments performed in this study, and other studies with hydrocarbon-contaminated aquifer material in which the utilization of aromatic hydrocarbons was much slower in the presence of a hydrocarbon phase (Hutchins, 1991a).

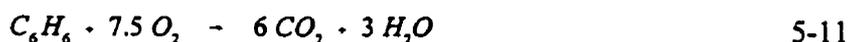
These field NO_3^- data may reflect an inhibitory effect associated with the gasoline phase. For example, toxicity may account for the lower NO_3^- utilization rate (0.2 mg/L/d) observed during the static period at the 60-cm depth interval. Toxicity effects in a microbial community adapted to hydrocarbons have been observed in other studies. Dibble and Bartha (1979) observed declining

microbial activity with increasing concentrations of oil sludge. The microbial community was already adapted to the hydrocarbon mixture; toxicity was manifested as a lower rate of substrate utilization. Other research has shown that microbial growth rates can be very slow in the presence of toxic compounds or conditions (Alexander, 1999). On the other hand, the range of uptake rates observed in the field is roughly equivalent to the rate observed by Barbaro et al. (1992) during biotransformation of low concentrations of aromatic hydrocarbons and other carbon compounds in the Borden landfill leachate plume. The lack of response to the addition of MBH medium indicated, as observed repeatedly in laboratory studies with Borden aquifer material, that anaerobic, denitrifying activity in the Nitrate Cell was not limited by inorganic nutrients.

Given the low rate of utilization and the nine-day residence time in the cell, anaerobic, denitrifying reactions did not appear to be important within the Nitrate Cell. However, to evaluate the potential of nitrate-based bioremediation, the specific denitrifying pathway was of some interest. The production of NO_2^- and apparent lack of other terminal electron-accepting processes in the treatment cell suggested that NO_3^- was utilized under anaerobic conditions primarily as an electron-acceptor in a dissimilatory reaction, rather than as a nitrogen source for cell protein. The specific pathway, denitrification or dissimilatory reduction of NO_3^- to ammonium (NH_4^+) (DRNA), was not defined *in situ*. Denitrification is generally assumed to be the predominant NO_3^- -reducing mechanism in carbon-limited environments, while DRNA may be favored under NO_3^- -limited conditions (i.e., in carbon-rich, anoxic environments) (Korom, 1992; Tiedje et al., 1982). DRNA has been identified as an important mechanism in contaminated aquifers (Bulger et al., 1989), but there are no reported cases of aromatic hydrocarbon utilization by this pathway. It should also be noted that autotrophic microbial denitrification coupled to the oxidation of sulfide minerals such as pyrite (Aravena and Robertson, 1998) and reduced Fe (Korom, 1992; Postma et al., 1991) has been reported recently. These reactions were not considered important in the Nitrate Cell, however, because minerals containing sulfide and reduced Fe are not prevalent in the Borden aquifer.

The O_2 mass balance results and assumed reactions were used to estimate the maximum mineralization that could occur under aerobic conditions. If the observed dissolved- O_2 threshold concentration was representative of *in situ* conditions, then only about 50-75% of the O_2 supplied to the aquifer for microaerophilic reactions was utilized. Even if all of the available O_2 was

utilized, however, the mass of O₂ added to the cells was probably insufficient to stimulate an observable removal of recalcitrant compounds such as benzene. For example, if aerobic benzene biotransformation is assumed to proceed completely to CO₂ with no assimilation of C by microbial cells (i.e., no growth), the mineralization reaction is



From the stoichiometry of this reaction, 3.1 g of O₂ are required to oxidize 1 g of benzene. Assuming that all of the injected and residual O₂ (ca. 300 g) in a given cell was used to mineralize benzene, then 97 grams or 15% of the 640 grams of benzene added to the cell would be removed. This is clearly an overestimate because O₂ would likely be utilized in the oxidation of other carbon compounds as well, including other aromatic hydrocarbons (Chapter 4). More realistically, if only a fraction (for example, one quarter) of the available O₂ was utilized for benzene oxidation, then only 24 grams of benzene would be removed. Assuming all of the available O₂ was consumed by the aromatic hydrocarbons (i.e., none was consumed in reactions with other gasoline hydrocarbons), 300 g O₂ would oxidize only 95 g total BTEXTMB to CO₂. Based on these assumed reactions, the calculated mass loss was very small relative to the initial mass in a given treatment cell. If biomass production is taken into account, less O₂ is required per mole of substrate oxidized (Wiedemeier et al., 1999), but the extent of mass loss would still be minor relative to the total mass in the cell. Therefore, if the addition of microaerophilic O₂ did contribute to the mineralization of the soluble compounds in the source area, the effect would probably have been very small in relation to the size of the carbon pool, and difficult to detect in the field.

The NO₃⁻ mass balance results were used in a similar manner to estimate the maximum mass loss from mineralization that could occur under denitrifying conditions. Although most of the NO₃⁻ consumed in the Nitrate Cell may have been utilized as an N source during aerobic biotransformation, and aromatic-hydrocarbon utilization under anaerobic conditions appeared low, some biotransformation of the more labile compounds may have occurred. Considering the relatively low NO₃⁻ uptake, these losses would also have been difficult to detect in the experimental system. For example, assuming toluene is mineralized to CO₂ by a denitrification reaction and there is no C or N assimilation by microbial cells (Equation 4-2), 446.4 g NO₃⁻ are

required to oxidize 92.1 g toluene. Stoichiometries of the other NO_3^- -reducing reactions (NO_2^- or N_2O end products) that may have occurred yield similar molar ratios. The 890 g of NO_3^- that were consumed over the 174-day flushing experiment (Table 5-4) therefore correspond to about 180 g toluene, or 7.8 % of the flushed mass (2300 g) and 4.5 % of the total mass (4,000 g) of toluene in the cell. This calculation overestimates toluene removal because it is based on the assumptions that all of the NO_3^- was consumed under anaerobic conditions with toluene as the sole substrate. Nonetheless, the calculated mass loss is still small relative to the size of the toluene pool, and would have been difficult to detect in the field.

The detection of metabolites demonstrated that some partial oxidation of gasoline hydrocarbons was occurring in both cells. The number of aromatic acids detected in the Nitrate Cell was substantially larger than in the Control Cell, perhaps reflecting a response to NO_3^- addition. A transformation to a partially-oxidized intermediate, such as benzoic acid, requires less O_2 per mole of parent compound oxidized. It is conceivable, therefore, that losses of aromatic hydrocarbons from biotransformation were more extensive than indicated by the mineralization reactions. If partial oxidation to a stable intermediate was occurring, reaction stoichiometries show that mass loss of a given constituent could have been substantial relative to the total mass in the cell. For example, again assuming no assimilation of C and N by microbial cells, the following reaction controls the partial oxidation of benzene to phenol (Cozzarelli et al., 1990),



Equation 5-12 shows that one gram of O_2 would partially-oxidize 4.9 g benzene, and if it is assumed that the maximum benefit was gained from microaerophilic O_2 addition (i.e., 100% partial oxidation of benzene), 300 g of O_2 would be sufficient to partially-oxidize 1470 g benzene, which exceeds the total benzene mass in the cell. More realistically, if it is arbitrarily assumed that only 25% of the total O_2 mass was consumed for benzene degradation, then 75 g would be available for reaction, which corresponds to a transformation of 367 g benzene to phenol, or approximately 50% of the initial benzene mass. Using similar reasoning, if toluene was transformed to benzoic acid under denitrifying conditions (Kuhn et al., 1988), then partial oxidation of toluene could produce substantial losses of toluene and production of benzoic acid.

These calculations suggest that if significant partial oxidation had occurred, losses from biotransformation would clearly have been observable in the treatment cells. However, based on the limited sampling performed here, low concentrations of metabolites appeared to be forming from a relatively large group of parent gasoline hydrocarbons, particularly in the Nitrate Cell, suggesting that these reactions were only of minor importance for the soluble aromatic compounds. Moreover, these metabolites may not have been persistent, in which case additional oxidant (i.e., O_2 or NO_3^-) would have been consumed to complete the reaction, and the stoichiometries of the mineralization reactions discussed above would be predominant. Regardless of the extent of mineralization, the low consumption of NO_3^- ; the limited mass of O_2 available for reaction, and the presence of multiple carbon sources that may have participated in the consumption of these electron acceptors indicate that mass losses of the aromatic hydrocarbons from biotransformation were very minor relative to total masses in both treatment cells. This conclusion was confirmed for the Nitrate Cell by the follow-up microcosm experiment, and was consistent with other field observations (e.g., similar concentration distributions between cells), and the numerical analyses performed on the measured breakthrough curves.

Although there was less biotransformation than anticipated, this field experiment did provide comprehensive gasoline dissolution data, obtained from well-defined sources under highly-controlled experimental conditions. The dissolution process was simulated to assist in the interpretation of the site-specific experimental results, and to gain a better general understanding of the effects of stimulating biotransformation in the proximity of a source area. To understand the net result of flushing fluid through a NAPL, consideration must be given to the complex interactions between dissolution and chemical reactions. If, for example, the biotransformation rate is low, soluble compounds may be removed from the source area by flushing before significant biotransformation occurs (Malone et al., 1993; Seagren et al., 1993; Seagren et al., 1994). Because the composition of the gasoline used in this study was very well defined, it was possible to use a simple model based on equilibrium partitioning to compare observed aqueous concentrations with concentrations in gasoline-saturated water as flushing proceeded. The results of this analysis clearly showed that aromatic-hydrocarbon concentrations exiting the treatment cells had not been reduced appreciably by reactions along the flowpath. Consequently, it appeared that, within this particular experimental system, electron-acceptor flushing did not lower the flux of soluble constituents from the gasoline-contaminated zone to the aquifer. More generally, because

transport parameters such as the dispersivity and retardation factor were found to be relatively unimportant over the short flowpath monitored in the treatment cells, the simulations performed here showed that it might be possible to analyze field data near source areas for evidence of biotransformation using very simple dissolution models based on equilibrium partitioning. The RME analysis also appeared to be a good tool for assessing the extent of reaction between a NAPL and a nearby monitoring point. In practice, however, reliable parameter estimation will limit these approaches at real spill sites.

6.0 CONCLUSIONS AND IMPLICATIONS

Generally the findings on the degradability of aromatic hydrocarbons in the presence of microaerophilic O_2 and NO_3^- were consistent between laboratory and field experiments: mass losses were minor in the Nitrate Cell as well as in both laboratory microcosm experiments in which conditions similar to the field were established (i.e., BTEXTMB concentrations near gasoline-saturated concentrations with microaerophilic O_2 and NO_3^- (Experiments 1 and 3)). As discussed in Chapter 5, however, ascertaining small mass losses in the field was difficult because of the size of the carbon pool and the uncertainty associated with the mass balance. The apparent lack of extensive mass losses in the field was also consistent with the results of the microbial enumerations performed in the laboratory. In both the field and the laboratory microcosm experiment with contaminated aquifer material, NO_3^- depletion was observed over time periods on the order of 100 days, but accompanying utilization of labile aromatic compounds was either not apparent or quite low. The use of NO_3^- solely as an electron acceptor was equivocal; utilization of some NO_3^- as an N source may have occurred under aerobic conditions. In both of these experimental systems, the effect of microaerophilic O_2 was small, although the disparity between static microcosms and dynamic field conditions makes the comparison tenuous. Perhaps most important for remediation, there was agreement on the minor benzene losses in the presence of microaerophilic O_2 .

Although there was evidence that microbial activity had been stimulated, the field and laboratory data indicated overall that nitrate-based bioremediation was not an effective source-area remedial technology in this aquifer. The field evidence for activity included 1) NO_3^- consumption and NO_2^- production, 2) O_2 consumption, and 3) metabolite production. However, NO_3^- utilization was slow relative to nine-day the residence time in the treatment cell, and, as mentioned above, preferential utilization of labile aromatic compounds was not apparent. It is not clear why a large denitrifying population capable of rapid aromatic-hydrocarbon biotransformation did not develop in the treatment cell in response to extended exposure to abundant substrate and NO_3^- . One possibility is that the denitrifying population was relatively sensitive to the presence of a gasoline phase, the associated high aqueous concentrations of the soluble hydrocarbons, or the metabolites of gasoline hydrocarbons, which slowed growth rates and metabolism. Another possibility that cannot be ruled out is that the observed O_2 threshold was real (i.e., not a sampling artifact), and

that this residual O₂ adversely affected NO₃⁻ utilization. The question of toxicity remains unanswered, however, because systematic experiments designed to identify the source(s) of the toxicity were not performed in this study.

In contrast to NO₃⁻, dissolved O₂ was consumed rapidly in both laboratory and field experiments, demonstrating that aerobic activity was not suppressed, but under microaerophilic conditions mass losses were limited by the quantity of O₂ available for reaction, and possibly by abiotic demand in the field. Based on the laboratory results, dissolved O₂ may have been used to oxidize compounds that otherwise would have been recalcitrant under anaerobic, denitrifying conditions, but *in situ* these losses appeared very limited relative to the mass of gasoline hydrocarbons in the cells. This suggests that the partial oxidation of the target compounds by microaerophilic O₂ was a relatively unimportant process in this system. In addition, there was no evidence that other terminal electron acceptors were being utilized in the treatment cells. As expected from these electron-acceptor trends, mass losses were not enhanced in the cell treated with microaerophilic O₂ and NO₃⁻ relative to the control, and effluent breakthrough curves in both cells were consistent with concentration trends expected to result from abiotic gasoline dissolution.

These conclusions pertain to the specific experimental system evaluated in this study (i.e., a recent gasoline spill flushed for a relatively short period of time and monitored over a short flow path). It is conceivable that this approach, particularly with respect to the effects of microaerophilic O₂, would be more effective during the latter stages of an enhanced bioremediation project when source-area concentrations were lower, or for downgradient plume control using a reactive wall or other semi-passive remedial technology. Similarly, although NO₃⁻ utilization was minor over the flowpath evaluated here, adaptation resulting in the development of a substantial population capable of degrading TEX may have occurred with continued exposure. Existing studies have indicated, however, that NO₃⁻ utilization rates are generally slow relative to O₂ utilization rates (Section 1.2.2). This suggests that a longer residence time would be more appropriate for evaluating the effects of NO₃⁻ addition. Based on existing data for this aquifer (e.g., Barbaro et al., 1992), it is possible that substantial NO₃⁻ utilization would have occurred further downgradient (beyond this experimental system) in the anaerobic core of the plume, providing some benefit by reducing the mass of carbon in the plume. Finally, the results reported here are specific to the Borden aquifer; generalization of the results to other sites is inadvisable without

site-specific testing. The comparison of aromatic hydrocarbon mass loss in both pristine and gasoline-contaminated Borden sediment with sediment from other petroleum-hydrocarbon-contaminated sites revealed a substantial range in the capabilities of the indigenous denitrifying populations (Barbaro et al., 1998).

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APPENDICES

APPENDIX A. GASOLINE CHARACTERISTICS

American Petroleum Institute (API) gasoline was used in all of the experiments in this study. This unleaded gasoline, designated 91-01, was used for various toxicological research programs. Consequently, comprehensive analytical work was done by the API in 1991 when the gasoline was formulated to define its composition and physical properties (raw data not shown). Although gasoline may contain more than 1,000 compounds (Brookman et al., 1985), a relatively small group accounts for most of the weight. Approximately 150 compounds and generic compound classes were identified in API 91-01, of which only 25 account for 65% of the gasoline weight (Table A-1). An accurate characterization of the gasoline composition was required to complete the field mass balance, and to predict dissolved aromatic hydrocarbon concentrations. Molar fractions for all identified compounds are compiled in Table A-1. Basic characteristics of the gasoline, including weight fractions of BTEXTMB, are summarized in Table A-2.

Several analyses were performed over the course of this study to verify the accuracy of the API weight fraction data. GC analyses (Appendix C) of known volumes of API 91-01 gasoline in methanol yielded weight fractions of aromatic hydrocarbons that agreed well with the API weight fractions listed in Tables A-1 and A-2. These analyses are summarized in Table A-3. All of the samples analyzed by the Organic Geochemistry Laboratory at the University of Waterloo were taken from an aliquot of API 91-01 stored in laboratory. The August, 1997 sample was submitted and analyzed with the core extract samples collected from the treatment cells. The August, 1998 samples were analyzed one year later to obtain additional gasoline composition data. Percent differences were less than approximately 20% for all compounds, with the exception of naphthalene (up to 40%).

Aqueous concentrations of BTEXTMB in gasoline-saturated water, measured in laboratory batch equilibrium tests, agreed well with concentrations calculated from Raoult's Law (Table A-4). Raoult's Law calculations were based on literature solubilities and the mole fractions listed in Table A-1. Calculated concentrations were lower than measured by ca. 20%, possibly because of non-ideal behavior in the gasoline phase (Borden and Kao, 1992). The reasonable agreement between measured and calculated concentrations indicated not only that the API weight-fraction

data were representative, but also that Raoult's Law could be used to describe equilibrium partitioning between the gasoline and groundwater (Eganhouse et al., 1996). These issues are discussed in greater detail in Section 5.3.

Table A-1. Mole fractions of identified compounds in API 91-01 gasoline. Compound identification and weight fractions compiled from an unpublished 1991 analysis of the gasoline performed by the API.

Compound	Carbon	Hydrogen	Wt.%	C x Wt%	H x Wt%	Mol. Wt. (g/mole)	wt%/mol. Wt. (moles/100g)	Mole Fraction
Propane	3	8	0.01	0.03	0.08	44.10	0.0002	0.00021
Isobutane	4	10	0.14	0.56	1.40	58.12	0.0024	0.00227
n-Butane	4	10	4.88	19.52	48.80	58.12	0.0840	0.07896
1,2-Butadiene	4	6	0.03	0.12	0.18	54.09	0.0006	0.00052
3-Methyl-1-butene	5	10	0.03	0.15	0.30	70.13	0.0004	0.00040
Isopentane	5	12	4.51	22.55	54.12	72.15	0.0625	0.05879
1-Pentene	5	10	0.63	3.15	6.30	70.13	0.0090	0.00845
n-Pentane	5	12	3.61	18.05	43.32	72.15	0.0500	0.04705
trans-2-Pentene	5	10	0.73	3.65	7.30	70.13	0.0104	0.00979
cis-2-Pentene	5	10	0.43	2.15	4.30	70.13	0.0061	0.00577
2-Methyl-2-butene	5	10	1.21	6.05	12.10	70.13	0.0173	0.01622
2,2-dimethylbutane	6	14	0.505	3.03	7.07	86.18	0.0059	0.00551
cyclopentadiene	5	6	0.505	2.53	3.03	66.10	0.0076	0.00718
cyclopentene	5	8	0.17	0.85	1.36	68.12	0.0025	0.00235
4-methyl-1-pentene	6	12	0.06	0.36	0.72	84.16	0.0007	0.00067
3-methyl-1-pentene	6	12	0.08	0.48	0.96	84.16	0.0010	0.00089
Cyclopentane	5	10	0.23	1.15	2.30	70.13	0.0033	0.00308
2,3-dimethylbutane	6	14	1.65	9.90	23.10	86.18	0.0191	0.01801
4-methyl-cis-2-pentene	6	12	0.06	0.36	0.72	84.16	0.0007	0.00067
2-methylpentane	6	14	5.52	33.12	77.28	86.18	0.0641	0.06024
4-methyl-trans-2-pentene	6	12	0.04	0.24	0.48	84.16	0.0005	0.00045
3-methylpentane	6	14	3.12	18.72	43.68	86.18	0.0362	0.03405
2-methyl-1-pentene	6	12	0.28	1.68	3.36	84.16	0.0033	0.00313
1-hexene	6	12	0.12	0.72	1.44	84.16	0.0014	0.00134
n-hexane	6	14	2.65	15.90	37.10	86.18	0.0308	0.02892
trans-3-hexene	6	12	0.18	1.08	2.16	84.16	0.0021	0.00201
trans-2-hexene	6	12	0.38	2.28	4.56	84.16	0.0045	0.00425
3-methyl-cis-2-pentene	6	12	0.11	0.66	1.32	84.16	0.0013	0.00123
4-methylcyclopentene	6	10	0.26	1.56	2.60	82.15	0.0032	0.00298
3-methyl-trans-2-pentene	6	12	0.05	0.30	0.60	84.16	0.0006	0.00056
cis-2-hexene	6	12	0.21	1.26	2.52	84.16	0.0025	0.00235
2,2-dimethylpentane	7	16	0.43	3.01	6.88	100.20	0.0043	0.00404
methylcyclopentane	6	12	1.11	6.66	13.32	84.16	0.0132	0.01240
2,4-dimethylpentane	7	16	0.69	4.83	11.04	100.20	0.0069	0.00648
1-methylcyclopentene	6	10	0.38	2.28	3.80	82.15	0.0046	0.00435
C7 olefin	7	14	0.01	0.07	0.14	98.19	0.0001	0.00010
benzene	6	6	1.22	7.32	7.32	78.11	0.0156	0.01469
3,3-dimethylpentane	7	16	0.14	0.98	2.24	100.20	0.0014	0.00131
cyclohexane	6	12	0.28	1.68	3.36	84.16	0.0033	0.00313
C7 cyclo-olefin/diolefin	7	12	0.06	0.42	0.72	96.17	0.0006	0.00059
C7 olefin	7	14	0.12	0.84	1.68	98.19	0.0012	0.00115
2-methylhexane	7	16	1.63	11.41	26.08	100.20	0.0163	0.01530
2,3-dimethylpentane	7	16	1.3	9.10	20.80	100.20	0.0130	0.01220
1,1-dimethylcyclopentane	7	14	0.04	0.28	0.56	98.19	0.0004	0.00038
3-methylhexane	7	16	1.7	11.90	27.20	100.20	0.0170	0.01595
C7 olefin	7	14	0.04	0.28	0.56	98.19	0.0004	0.00038
trans-1,3-dimethylcyclopentane	7	14	0.32	2.24	4.48	98.19	0.0033	0.00306
cis-1,3-dimethylcyclopentane	7	14	0.28	1.96	3.92	98.19	0.0029	0.00268
3-ethylpentane	7	16	0.235	1.65	3.76	100.20	0.0023	0.00221
C7 olefin	7	14	0.235	1.65	3.29	98.19	0.0024	0.00225
trans-1,2-dimethylcyclopentane	7	14	1.76	12.32	24.64	98.19	0.0179	0.01686
2,2,4-trimethylpentane	8	18	0.105	0.84	1.89	114.23	0.0009	0.00086
C7 olefin	7	14	0.105	0.74	1.47	98.19	0.0011	0.00101
C7 olefin	7	14	0.11	0.77	1.54	98.19	0.0011	0.00105
n-heptane	7	16	1.3	9.10	20.80	100.20	0.0130	0.01220
C7 olefin	7	14	0.05	0.35	0.70	98.19	0.0005	0.00048

Table A-1. Mole fractions of identified compounds in API 91-01 gasoline. Compound identification and weight fractions compiled from an unpublished 1991 analysis of the gasoline performed by the API.

Compound	Carbon	Hydrogen	Wt.%	C x Wt%	H x Wt%	Mol. Wt. (g/mole)	wt%/mol. Wt. (moles/100g)	Mole Fraction
C7 olefin	7	14	0.24	1.68	3.36	98.19	0.0024	0.00230
C7 olefin	7	14	0.11	0.77	1.54	98.19	0.0011	0.00105
C7 olefin	7	14	0.12	0.84	1.68	98.19	0.0012	0.00115
C7 olefin	7	14	0.06	0.42	0.84	98.19	0.0006	0.00057
C7 olefin	7	14	0.13	0.91	1.82	98.19	0.0013	0.00125
C8 olefin	8	16	0.09	0.72	1.44	112.21	0.0008	0.00075
C8 olefin	8	16	0.09	0.72	1.44	112.21	0.0008	0.00075
C8 olefin	8	16	0.08	0.64	1.28	112.21	0.0007	0.00067
C8 olefin	8	16	0.05	0.40	0.80	112.21	0.0004	0.00042
cis-1,2-dimethylcyclopentane	7	14	0.18	1.26	2.52	98.19	0.0018	0.00172
methylcyclopentane	6	12	0.43	2.58	5.16	84.16	0.0051	0.00480
ethylcyclopentane	7	14	0.46	3.22	6.44	98.19	0.0047	0.00441
2,2,3-trimethylpentane	8	18	0.18	1.44	3.24	114.23	0.0016	0.00148
C8 olefin	8	16	0.19	1.52	3.04	112.21	0.0017	0.00159
2,4-dimethylhexane	8	18	0.18	1.44	3.24	114.23	0.0016	0.00148
C8 olefin	8	16	0.06	0.48	0.96	112.21	0.0005	0.00050
1,2,3-trimethylcyclopentane	8	16	0.05	0.40	0.80	112.21	0.0004	0.00042
C8 cyclo-olefin/diolefin	8	14	0.05	0.40	0.70	110.20	0.0005	0.00043
2,3,4-trimethylpentane	8	18	0.365	2.92	6.57	114.23	0.0032	0.00300
C8 olefin	8	16	0.365	2.92	5.84	112.21	0.0033	0.00306
toluene	7	8	7.68	53.76	61.44	92.14	0.0834	0.07839
2,3-dimethylhexane	8	18	0.205	1.64	3.69	114.23	0.0018	0.00169
C8 olefin	8	16	0.205	1.64	3.28	112.21	0.0018	0.00172
2-methylheptane	8	18	0.85	6.80	15.30	114.23	0.0074	0.00700
4-methylheptane	8	18	0.36	2.88	6.48	114.23	0.0032	0.00296
3-methylheptane	8	18	0.02	0.16	0.36	114.23	0.0002	0.00016
3-ethylhexane	8	18	0.605	4.84	10.89	114.23	0.0053	0.00498
C8 olefin	8	16	0.605	4.84	9.68	112.21	0.0054	0.00507
C8 Naphthene	8	16	0.07	0.56	1.12	112.21	0.0006	0.00059
C8 olefin	8	16	0.07	0.56	1.12	112.21	0.0006	0.00059
C8 Naphthene	8	16	0.08	0.64	1.28	112.21	0.0007	0.00067
C8 olefin	8	16	0.08	0.64	1.28	112.21	0.0007	0.00067
C8 Naphthene	8	16	0.065	0.52	1.04	112.21	0.0006	0.00054
C8 olefin	8	16	0.065	0.52	1.04	112.21	0.0006	0.00054
C8 Naphthene	8	16	0.09	0.72	1.44	112.21	0.0008	0.00075
C8 Naphthene	8	16	0.13	1.04	2.08	112.21	0.0012	0.00109
n-octane	8	18	0.65	5.20	11.70	114.23	0.0057	0.00535
trans-1,2-dimethylcyclohexane	8	16	0.12	0.96	1.92	112.21	0.0011	0.00101
C8 olefin	8	16	0.05	0.40	0.80	112.21	0.0004	0.00042
C9 naphthene	9	18	0.21	1.89	3.78	126.24	0.0017	0.00156
C9 paraffin	9	20	0.025	0.23	0.50	128.26	0.0002	0.00018
C8 olefin	8	16	0.025	0.20	0.40	112.21	0.0002	0.00021
C8 olefin	8	16	0.06	0.48	0.96	112.21	0.0005	0.00050
C9 paraffin	9	20	0.19	1.71	3.80	128.26	0.0015	0.00139
cis-1,2-dimethylcyclohexane	8	16	0.025	0.20	0.40	112.21	0.0002	0.00021
C9 olefin	9	18	0.025	0.23	0.45	126.24	0.0002	0.00019
C9 paraffin	9	20	0.03	0.27	0.60	128.26	0.0002	0.00022
C9 naphthene	9	18	0.03	0.27	0.54	126.24	0.0002	0.00022
Ethylbenzene	8	10	3.37	26.96	33.70	106.17	0.0317	0.02985
m-Xylene	8	10	5.31	42.48	53.10	106.17	0.0500	0.04704
p-Xylene	8	10	2.13	17.04	21.30	106.17	0.0201	0.01887
2-methyloctane	9	20	0.28	2.52	5.60	128.26	0.0022	0.00205
4-methyloctane	9	20	0.32	2.88	6.40	128.26	0.0025	0.00235
3-methyloctane	9	20	0.34	3.06	6.80	128.26	0.0027	0.00249
o-Xylene	8	10	2.64	21.12	26.40	106.17	0.0249	0.02339
C10 naphthene	10	20	0.04	0.40	0.80	140.27	0.0003	0.00027

Table A-1. Mole fractions of identified compounds in API 91-01 gasoline. Compound identification and weight fractions compiled from an unpublished 1991 analysis of the gasoline performed by the API.

Compound	Carbon	Hydrogen	Wt.%	C x Wt%	H x Wt%	Mol. Wt. (g/mole)	wt%/mol. Wt. (moles/100g)	Mole Fraction
n-nonane	9	20	0.24	2.16	4.80	128.26	0.0019	0.00176
C9 naphthene	9	18	0.02	0.18	0.36	126.24	0.0002	0.00015
isopropylbenzene	9	12	0.22	1.98	2.64	120.19	0.0018	0.00172
C9 naphthene	9	18	0.02	0.18	0.36	126.24	0.0002	0.00015
n-propylbenzene	9	12	0.75	6.75	9.00	120.19	0.0062	0.00587
1-methyl-3-ethyl-benzene	9	12	2.34	21.06	28.08	120.19	0.0195	0.01831
1-methyl-4-ethyl-benzene	9	12	1.06	9.54	12.72	120.19	0.0088	0.00829
C10 paraffin	10	22	0.03	0.30	0.66	142.28	0.0002	0.00020
1,3,5-trimethylbenzene	9	12	1.1	9.90	13.20	120.19	0.0092	0.00861
4-methylnonane	10	22	0.11	1.10	2.42	142.28	0.0008	0.00073
2-methylnonane	10	22	0.15	1.50	3.30	142.28	0.0011	0.00099
1-methyl-2-ethylbenzene	9	12	0.72	6.48	8.64	120.19	0.0060	0.00563
1,2,4-trimethylbenzene	9	12	3.37	30.33	40.44	120.19	0.0280	0.02637
1,2,3-trimethylbenzene	9	12	0.68	6.12	8.16	120.19	0.0057	0.00532
Indane	10	26	0.4	4.00	10.40	146.32	0.0027	0.00257
C11 paraffin	11	24	0.05	0.55	1.20	156.31	0.0003	0.00030
C11 paraffin	11	24	0.22	2.42	5.28	156.31	0.0014	0.00132
1-methyl-3-n-propylbenzene	10	14	0.48	4.80	6.72	134.22	0.0036	0.00336
1-methyl-4-n-propylbenzene	10	14	0.28	2.80	3.92	134.22	0.0021	0.00196
n-butylbenzene	10	14	0.14	1.40	1.96	134.22	0.0010	0.00098
1,2-diethylbenzene	10	14	0.44	4.40	6.16	134.22	0.0033	0.00308
1,3-dimethyl-5-ethylbenzene	10	14	0.02	0.20	0.28	134.22	0.0001	0.00014
1,4-diethylbenzene	10	14	0.02	0.20	0.28	134.22	0.0001	0.00014
C11 paraffin	11	24	0.01	0.11	0.24	156.31	0.0001	0.00006
1,3-dimethyl-4-ethylbenzene	10	14	0.125	1.25	1.75	134.22	0.0009	0.00088
Indane	10	26	0.125	1.25	3.25	146.32	0.0009	0.00080
1,2-dimethyl-4-ethylbenzene	10	14	0.31	3.10	4.34	134.22	0.0023	0.00217
Indane	10	26	0.31	3.10	8.06	146.32	0.0021	0.00199
1,2-dimethyl-3-ethylbenzene	10	14	0.15	1.50	2.10	134.22	0.0011	0.00105
n-undecane	11	24	0.06	0.66	1.44	156.31	0.0004	0.00036
1,2,4,5-tetramethylbenzene	10	14	0.24	2.40	3.36	134.22	0.0018	0.00168
1,2,3,5-tetramethylbenzene	10	14	0.33	3.30	4.62	134.22	0.0025	0.00231
dodecane	12	26	0.05	0.60	1.30	170.34	0.0003	0.00028
Naphthalene	10	8	0.53	5.30	4.24	128.17	0.0041	0.00389
C13 paraffins	13	28	0.19	2.47	5.32	184.36	0.0010	0.00097
C12 aromatics	12	18	1.06	12.72	19.08	162.27	0.0065	0.00614
C12 Indanes	10	26	0.54	5.40	14.04	146.32	0.0037	0.00347
Methylnaphthalenes	11	12	0.69	7.59	8.28	144.22	0.0048	0.00450
Unidentified heavies	12	26	0.99	11.88	25.74	170.34	0.0058	0.00547
unknowns	7	16	4.86	34.02	77.76	100.20	0.0485	0.04561
TOTAL			100.00				1.0633	1.00000

Calculated molecular weight: 94.0 g/mole

c8, c9, and c10 naphthene molecular weights taken from Table 2-A Poulson et. al. (1990).
 Indanes taken from same source. Assumed average group molecular weight.
 Assumed value near gasoline molecular weight for unknown fraction.
 Assumed dodecane molecular weight for unknown heavies.

Table A-2. Characteristics of API 91-01 gasoline.

Molecular Weight	(g/mole)	94.3
Density	(g/cm ³)	0.747
MTBE	(vol %)	<0.10
Methanol	(vol %)	<0.10
HYDROCARBON CLASSES (wt %)		
Paraffins		41.01
Naphthenes		6.84
Aromatics		39.05
Olefins		11.74
Unknowns		1.26
AROMATIC HYDROCARBONS (wt % (mole fraction))		
Benzene		1.22 (0.0147)
Toluene		7.68 (0.0787)
Ethylbenzene		3.37 (0.0300)
<i>m</i> -Xylene		5.31 (0.0472)
<i>p</i> -Xylene		2.13 (0.0189)
<i>o</i> -Xylene		2.64 (0.0235)
1,3,5-Trimethylbenzene		1.10 (0.00864)
1,2,4-Trimethylbenzene		3.37 (0.0265)
1,2,3-Trimethylbenzene		0.68 (0.00534)
Naphthalene		0.53 (0.00390)

Gasoline density measured at University of Waterloo (Oliveira, 1997). All other information from an unpublished 1991 analysis of the gasoline performed by API.

Table A-3. Comparison of measured concentrations of aromatic hydrocarbons in API 91-01 gasoline. All concentrations expressed weight percent.

Compound	API	This Study			
	(1991)	(August, 1997)	(August, 1998)	(August, 1998)	(August, 1998)
Benzene	1.22	1.28	1.02	0.96	0.97
Toluene	7.68	8.26	8.67	8.31	8.21
Ethylbenzene	3.37	3.48	3.50	3.33	3.30
<i>m+p</i> -Xylene	7.44	7.50	8.06	7.66	7.60
<i>o</i> -Xylene	2.64	2.70	2.75	2.61	2.59
1,3,5-Trimethylbenzene	1.10	1.13	1.18	1.12	1.11
1,2,4-Trimethylbenzene	3.37	3.02	3.18	3.01	2.97
1,2,3-Trimethylbenzene	0.68	0.67	0.74	0.70	0.69
Naphthalene	0.53	0.66	0.74	0.70	0.69

Samples analyzed August, 1998 are means of three injections.

Table A-4. Measured and calculated concentrations of aromatic hydrocarbons in water equilibrated with API 91-01 gasoline at 10°C.

Compound	Concentration (mg/L)		
	Measured	Calculated	% Diff
Benzene	30.90	26.25	15.1
Toluene	49.72	42.10	15.3
Ethylbenzene	6.41	5.42	15.3
<i>m+p</i> Xylene	13.45	10.59	21.3
<i>o</i> -Xylene	5.79	4.18	27.8
1,3,5-Trimethylbenzene	0.54	0.42	23.2
1,2,4-Trimethylbenzene	1.89	1.56	17.3
1,2,3-Trimethylbenzene	0.51	0.40	20.7
Naphthalene	0.84	0.63	24.7

Measured concentrations are means of four replicates collected from two separatory funnels. Coefficients of variation ranged from 1.3% (toluene) to 11% (naphthalene).

Calculated concentrations are based on Raoult's Law, $C_i = X_i S$, where X is the mole fraction of component i (Table A-1), S is the pure-phase solubility, and C is the calculated equilibrium concentration. Solubilities were obtained from published sources: benzene 1780 mg/L; toluene 535 mg/L; *p*-xylene 160 mg/L; *o*-xylene 178 mg/L; 1,3,5-trimethylbenzene 48 mg/L; 1,2,4-trimethylbenzene 59 mg/L; 1,2,3-trimethylbenzene 75 mg/L; naphthalene 161 mg/L (Sources: References cited within Montgomery (1996). The supercooled liquid solubility of naphthalene at 10°C was obtained from Equation 7 of Mackay et al. (1991)).

Percent difference:
$$\frac{(C_{meas} - C_{calc})}{C_{meas}} \cdot 100$$

APPENDIX B. TRACER TEST

B.1 Introduction

Tracer tests were performed in both treatment cells during the month of July, 1996 while the flushing experiment was in progress. The objectives of the test were to confirm that the injected water was distributed uniformly in the cells, and to calculate linear groundwater velocities and longitudinal dispersivities at different locations within the cells. Bromide (Br^-) was used as the conservative tracer.

B.2 Methods

A concentrated Br^- solution (ca. 26,000 mg/L) was prepared with KBr salt. The solution was pumped into the injection flow lines of both cells. A peristaltic pump (Masterflex L/S Series) equipped with an Ismatec multichannel head was used to feed the stock solution into the flow lines. The pumping rate was calibrated to a rate that yielded a 100x dilution of the concentrated solution. Brominated water was pumped into the cells over a 45 hour period to create a slug input. Injection water to each cell was sampled periodically to determine the mean injection concentrations (C_0).

In addition to injection samples, groundwater samples were collected periodically from all of the 60-cm, 120-cm, and 180-cm bgs piezometer ports, and the extraction-well sampling ports. These data were used to develop normalized concentration vs. time breakthrough curves (BTCs) at each sampling location. A plastic 60-cc syringe was used to collect groundwater samples from the piezometers. Prior to collecting a sample, about 20-ml water were removed to clear stagnant water from the piezometer tube and to flush the syringe. Samples from the injection flow lines were collected by holding the sample vial under the flowing stream of water at the tube outlet. Samples from the extraction flow lines were collected from the in-line sampling ports (see Figure 3-6). Once sampling began at a given depth, samples were collected approximately every six hours. A total of 540 samples was collected over a 400 hr period, and stored in plastic scintillation vials for analysis.

Samples were screened on-site with a conductivity meter. These data were used to monitor the position of the tracer slug as the test progressed. The goal was to obtain complete breakthrough curves for each piezometer port and the extraction wells. After the test, samples were returned to the laboratory and analyzed with a bromide-specific electrode (Corning, Model 476128). Samples were prepared for analysis by adding 5 ml ionic strength adjuster (0.2 M KNO₃ solution) to a 5 ml groundwater sample. Standards were prepared from a concentrated KBr stock solution, and diluted to the appropriate concentrations using aerobic Borden groundwater and 5 ml ionic strength adjuster. Each day, standards were run in duplicate or triplicate to generate a standard curve. Sample quantification was based on a linear regression of electrode response (mV) vs. natural log of the standard concentration. To check the accuracy of the Br⁻ electrode results, a subset of the groundwater samples analyzed on different days with the electrode was submitted to the Water Quality Laboratory for analysis by ion chromatography (see Section 3.6.5). As shown in Table B-1, there was good agreement between methods.

B.3 Results

Injection Br⁻ concentrations and extraction well BTCs are shown in Figures B-1 and B-2 for the Control and Nitrate Cells, respectively. Breakthrough curves from piezometer ports at the 60-, 120- and 180-cm depths of both experimental cells are shown in Figures B-3 through B-8. Based on eight samples, the average injection concentrations of the Br⁻ slug, C₀, were 260.1 ± 9 mg/L and 260.1 ± 12.4 mg/L for the Nitrate and Control Cells, respectively. As shown on the figures, complete BTCs were obtained for nearly all piezometer ports monitored during the test; in some cases (e.g., PZ3C-4, PZ3D-4), the initial arrival of the tracer slug was missed. The shapes of the BTCs were quite similar at a given depth, and there were no indicators (e.g., very early arrival of tracer) of short-circuiting along piezometer casings.

Linear groundwater velocities and dispersivities were calculated from breakthrough data at all 120- and 180-cm piezometer ports, and the extraction-well sampling ports. These parameters were obtained by fitting the one-dimensional advection-dispersion equation to the normalized BTCs. Modeling was done with Wpulsepe (Devlin and Barker, 1996; Sorel et al., 1998). This program uses a simplex optimization routine to find the best fit of the model solution to the data. The model requires only the length of the flowpath, the mean injection concentration, and the

concentration vs. time breakthrough data as input. The lengths of the flow paths were calculated assuming the upper head remained at 50-cm bgs during the test (70 cm and 130 cm flow paths for 120- and 180-cm bgs piezometer ports, respectively, and 175 cm to the midpoint of the extraction-well screens). Both velocity and dispersivity are used by the model as fitting parameters. As shown in the figures, the model fit the measured breakthrough data very well at most sampling locations.

Model-calculated velocities and dispersivities are shown in Table B-2. Velocities ranged from 0.45 cm/hr to 1.2 cm/hr and were consistent with a 200 ml/min injection rate. The velocities from piezometer BTCs represent the average rate of flow of the tracer in the individual flow tube intersecting the sample port. If sufficient ports are measured to obtain a representative sample of all of the flow tubes in the domain, the mean should be equal to the volumetric tracer injection rate. For this test, the expected linear velocity of 0.91 cm/hr (assumed porosity of 0.33) did fall within the error of the mean velocities calculated from piezometer breakthrough data in both cells (Table B-2). The velocities at the extraction wells were slightly higher, possibly reflecting the influence of the early arrival of Br⁻ in the faster flow tubes. Dispersivities were in the millimeter range in the Control Cell, and the millimeter to centimeter range in the Nitrate Cell (Table B-2). The largest dispersivities were measured at the extraction wells. These large dispersivities were likely caused by an integration of variable tracer concentrations along the 50-cm well screens as flow converged on the extraction wells (Sorel et al., 1998). Due to the radial flow patterns in the vicinity of the extraction wells, there was variability in the lengths of the flowpaths to these wells; flowpaths along the outer edges of the cells were substantially longer than those near the cell centers. The one-dimensional flow assumption is clearly an oversimplification of the flow field near the extraction wells. This issue is addressed in greater detail in Section 5.3.

Table B-1. Comparison of bromide concentrations determined from a bromide electrode and ion chromatography (IC). Concentrations in mg/L.

Sample	IC	Electrode
T-24	155.0	154.6
T-41	3.8	4.3
T-50	250.0	246.7
T-84	258.0	260.8
T-108	<0.05	0.6
T-126	7.8	7.8
T-131	44.4	40.9
T-160	222.0	223.5
T-175	0.21	1.1
T-216	289.0	292.8
T-284	1.3	1.5
T-314	62.8	67.1
T-349	293.0	277.8
T-406	87.1	88.5

Table B-2. Bromide tracer test results. Velocities and dispersivities calculated by fitting Wpulsepe to bromide breakthrough data.

Location	Vertical Distance (cm)	Velocity (cm/hr)	Dispersivity (cm)
Control Cell			
PZ3A-4	70	1.08	0.17
PZ3B-4	70	0.97	0.31
PZ3C-4	70	1.23	0.35
PZ3D-4	70	1.12	0.33
PZ3E-4	70	0.95	0.17
PZ3A-6	130	0.72	0.32
PZ3B-6	130	0.59	0.30
PZ3C-6	130	0.84	0.32
PZ3D-6	130	0.71	0.81
PZ3E-6	130	0.81	0.13
Extraction Well	175 ¹	1.29	13.45
MEAN (s.d.)		0.90 (0.2)	0.32 (0.19)
Nitrate Cell			
PZ4A-4	70	0.66	0.46
PZ4B-4	70	0.97	0.08
PZ4C-4	70	0.77	0.06
PZ4D-4	70	1.00	0.17
PZ4A-6	130	0.45	0.75
PZ4B-6	130	0.80	0.11
PZ4C-6	130	0.63	2.13
PZ4D-6	130	0.60	1.08
PZ4E-6	130	1.13	0.26
Extraction Well	175 ¹	1.21	5.26
MEAN (s.d.)		0.78 (0.22)	0.57 (0.68)

¹Distance to center of well screen.

Mean velocities and dispersivities do not include extraction well values.

Vertical distances calculated assuming upper head at 50 cm bgs during test.

Bromide Breakthrough Curves - Nitrate Cell

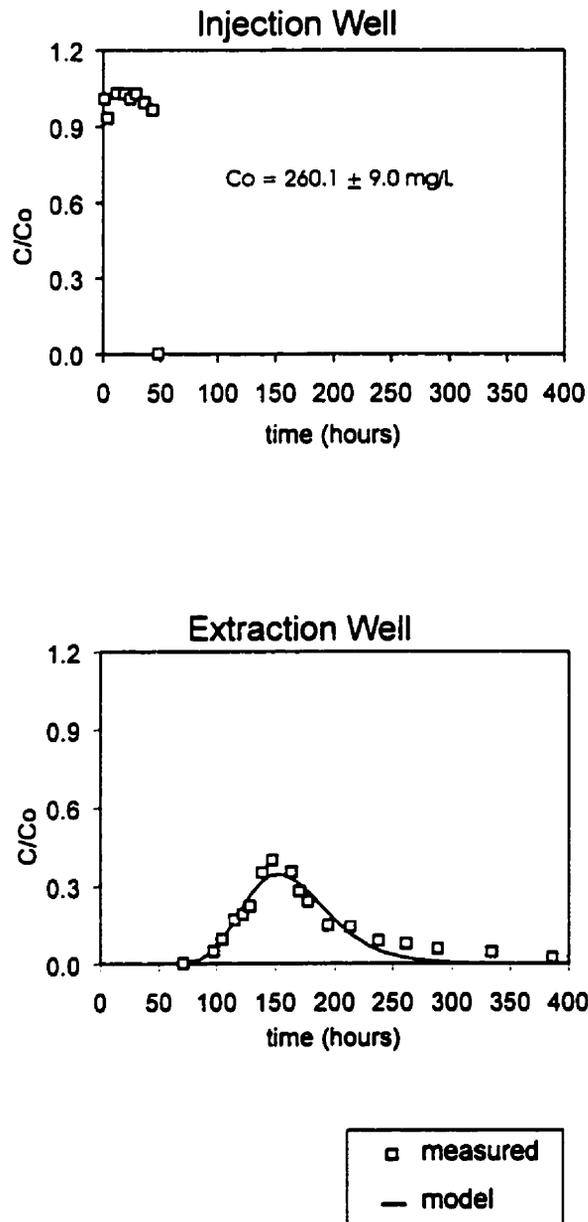


Figure B-1. Normalized bromide concentrations in samples of injection and extraction water during bromide tracer test (Nitrate Cell).

Bromide Breakthrough Curves - Control Cell

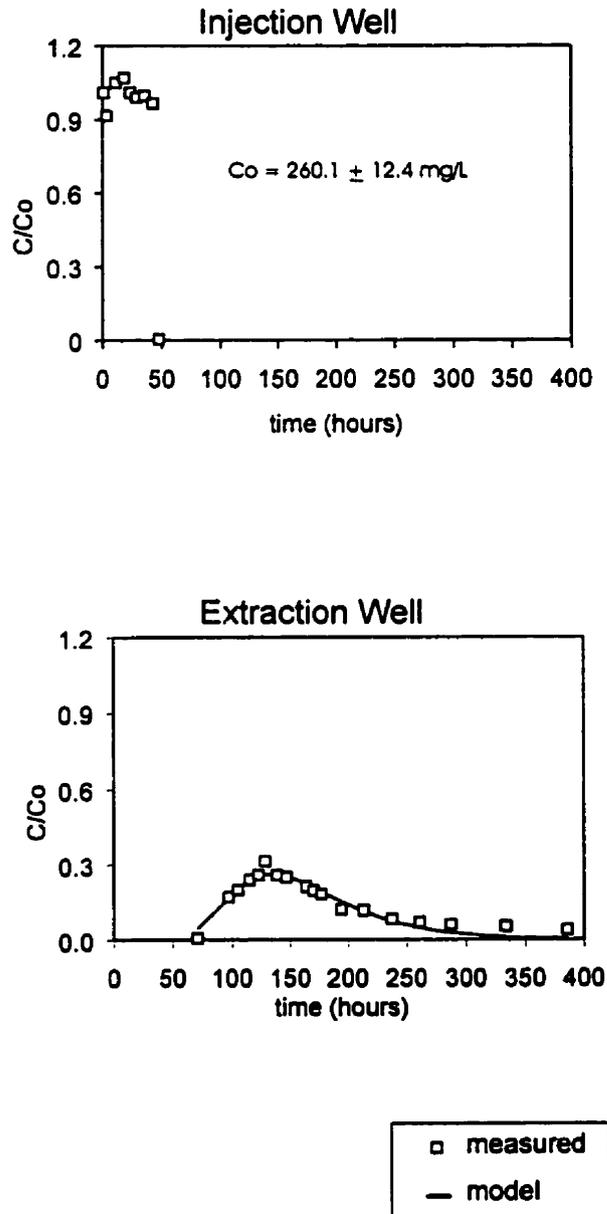


Figure B-2. Normalized bromide concentrations in samples of injection and extraction water during bromide tracer test (Control Cell).

Bromide Breakthrough Curves - Nitrate Cell, 60 cm Depth

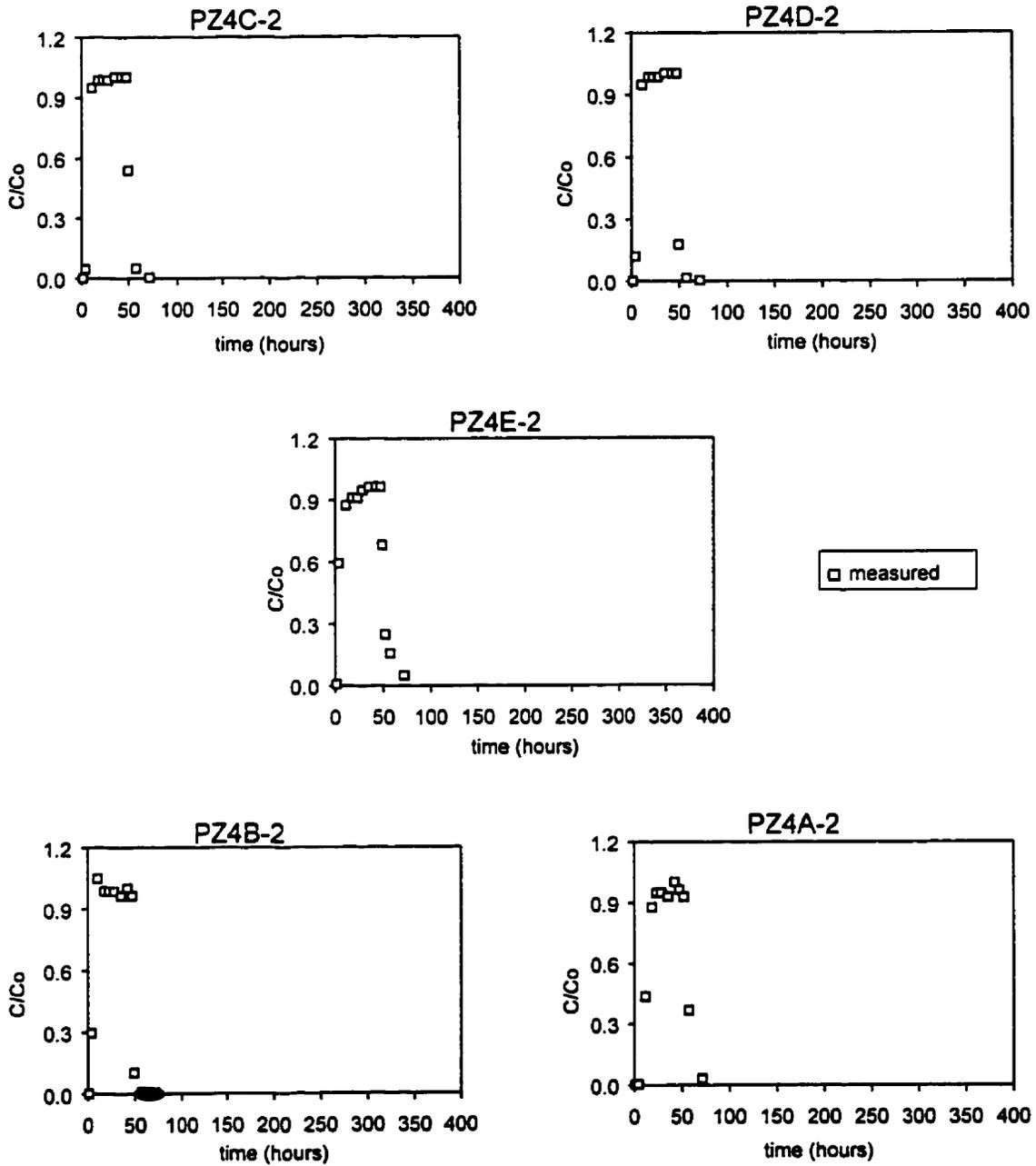


Figure B-3. Measured bromide breakthrough curves at 60-cm bgs ports in the Nitrate Cell.

Bromide Breakthrough Curves - Nitrate Cell, 120 cm Depth

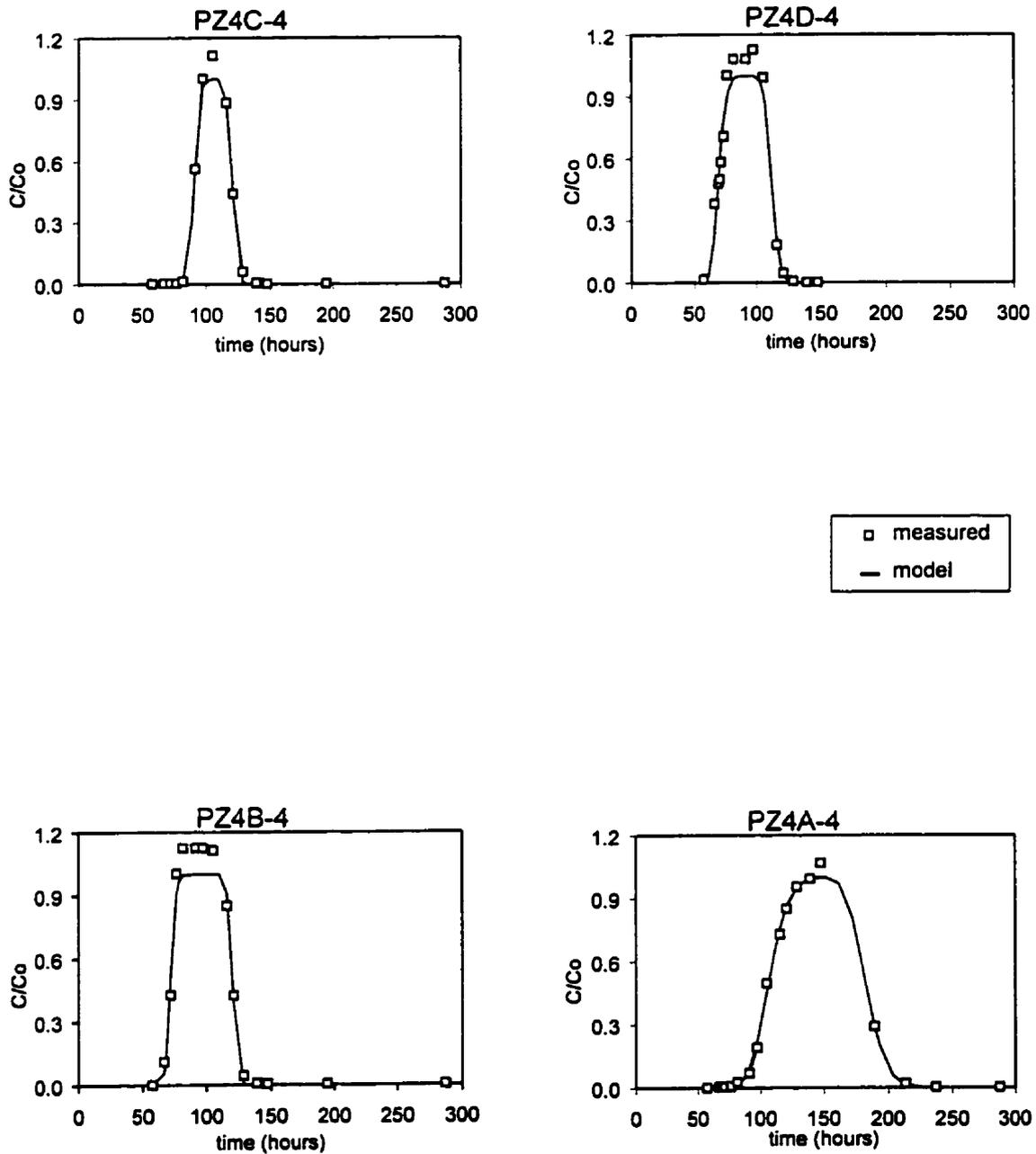


Figure B-4. Measured and calculated bromide breakthrough curves at 120-cm bgs ports in the Nitrate Cell. Samples could not be collected from the 120 cm port on the center piezometer (PZ4E-4).

Bromide Breakthrough Curves - Nitrate Cell, 180 cm Depth

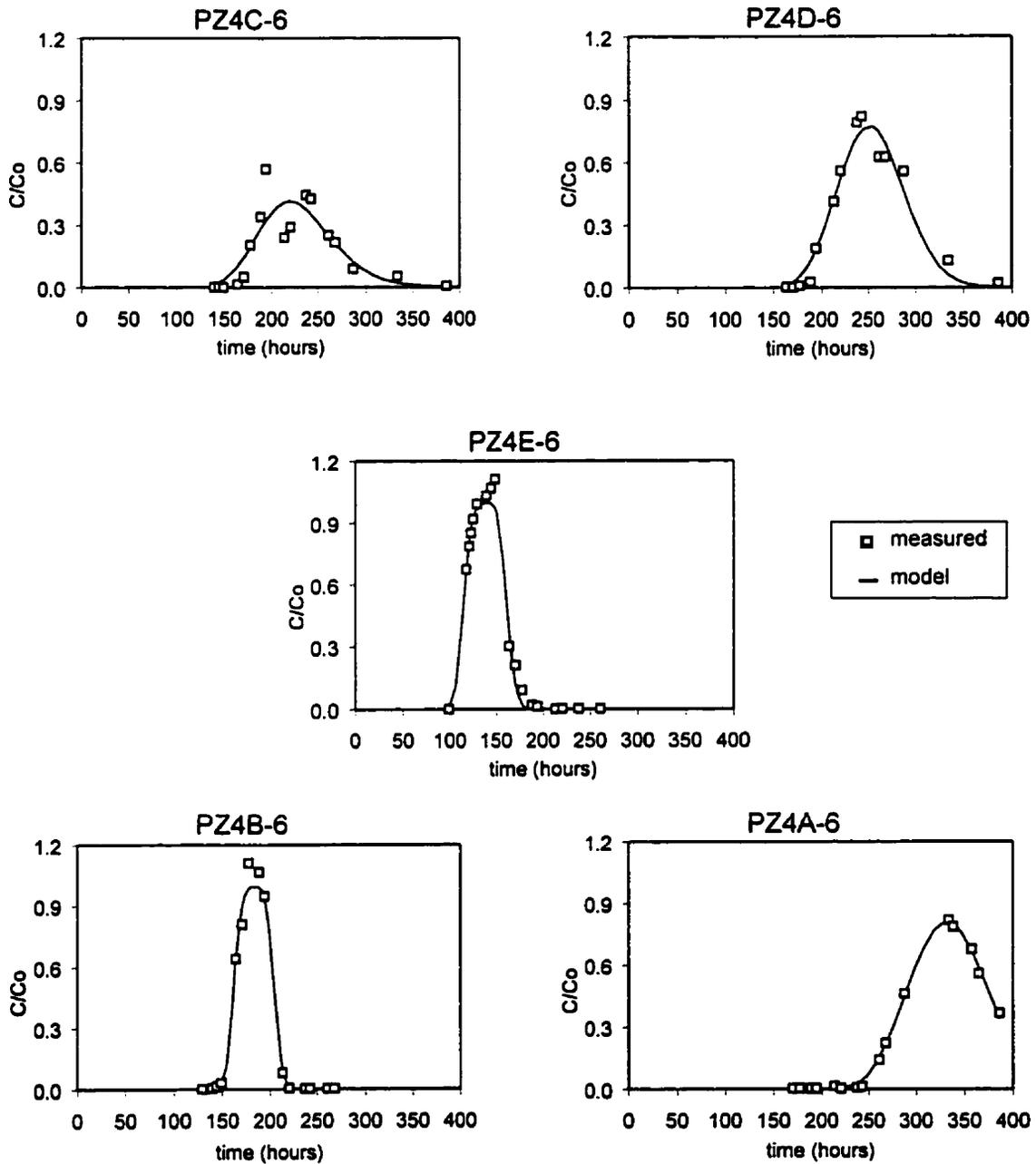


Figure B-5. Measured and calculated bromide breakthrough curves at 180-cm bgs ports in the Nitrate Cell.

Bromide Breakthrough Curves - Control Cell, 60 cm Depth

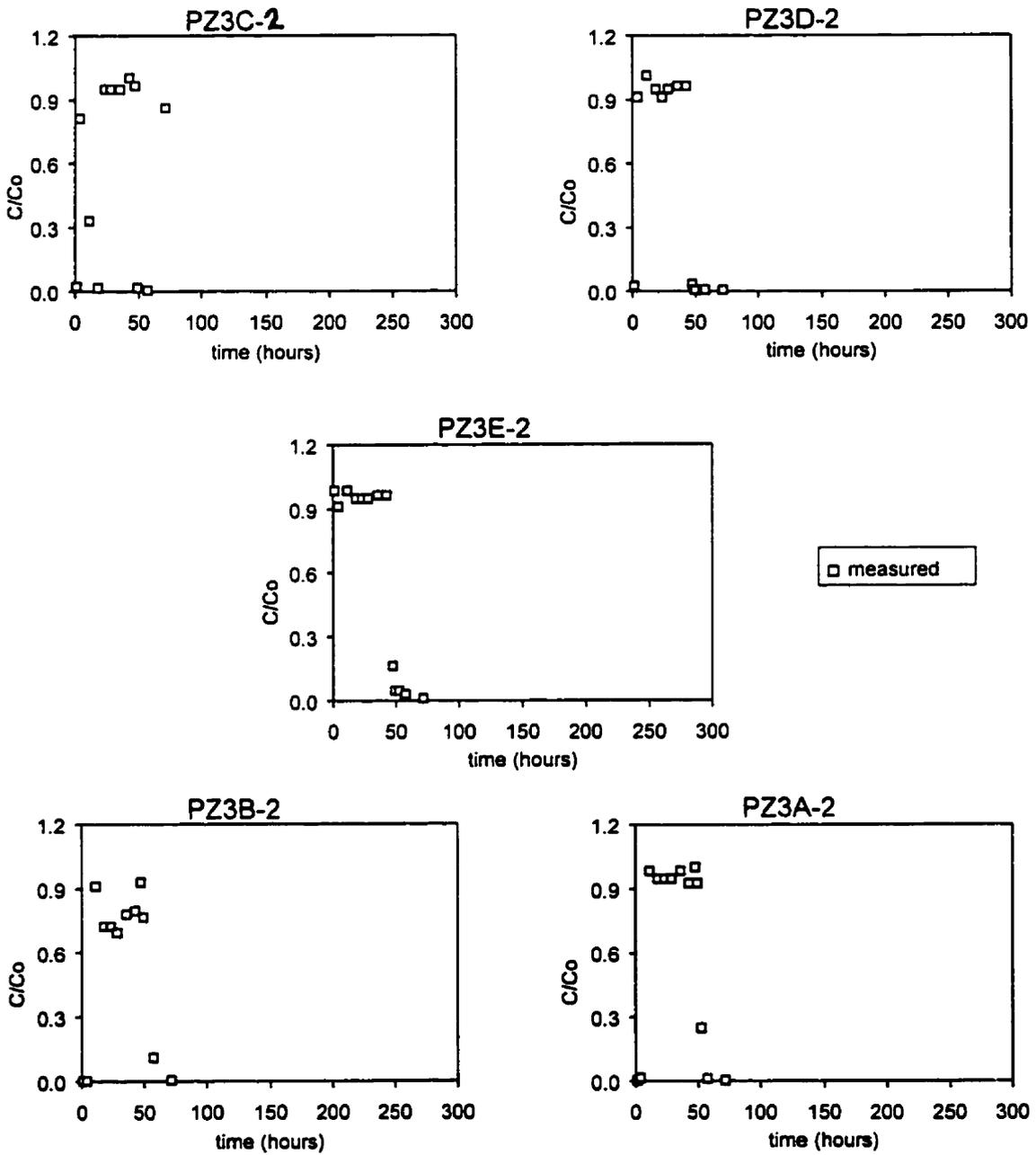


Figure B-6. Measured bromide breakthrough curves at 60-cm bgs ports in the Control Cell.

Bromide Breakthrough Curves - Control Cell, 120 cm Depth

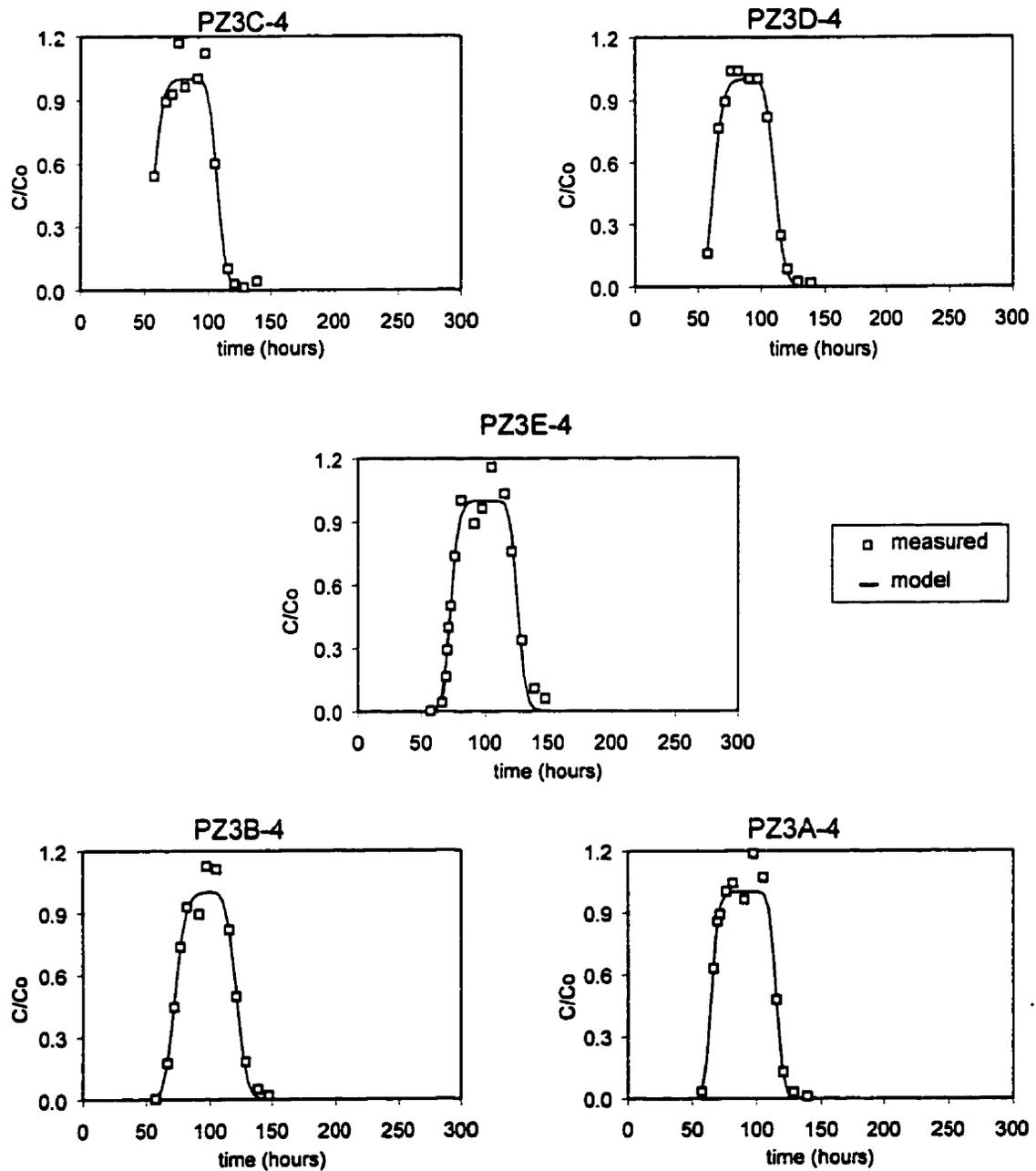


Figure B-7. Measured and calculated bromide breakthrough curves at 120-cm bgs ports in the Control Cell.

Bromide Breakthrough Curves - Control Cell, 180 cm Depth

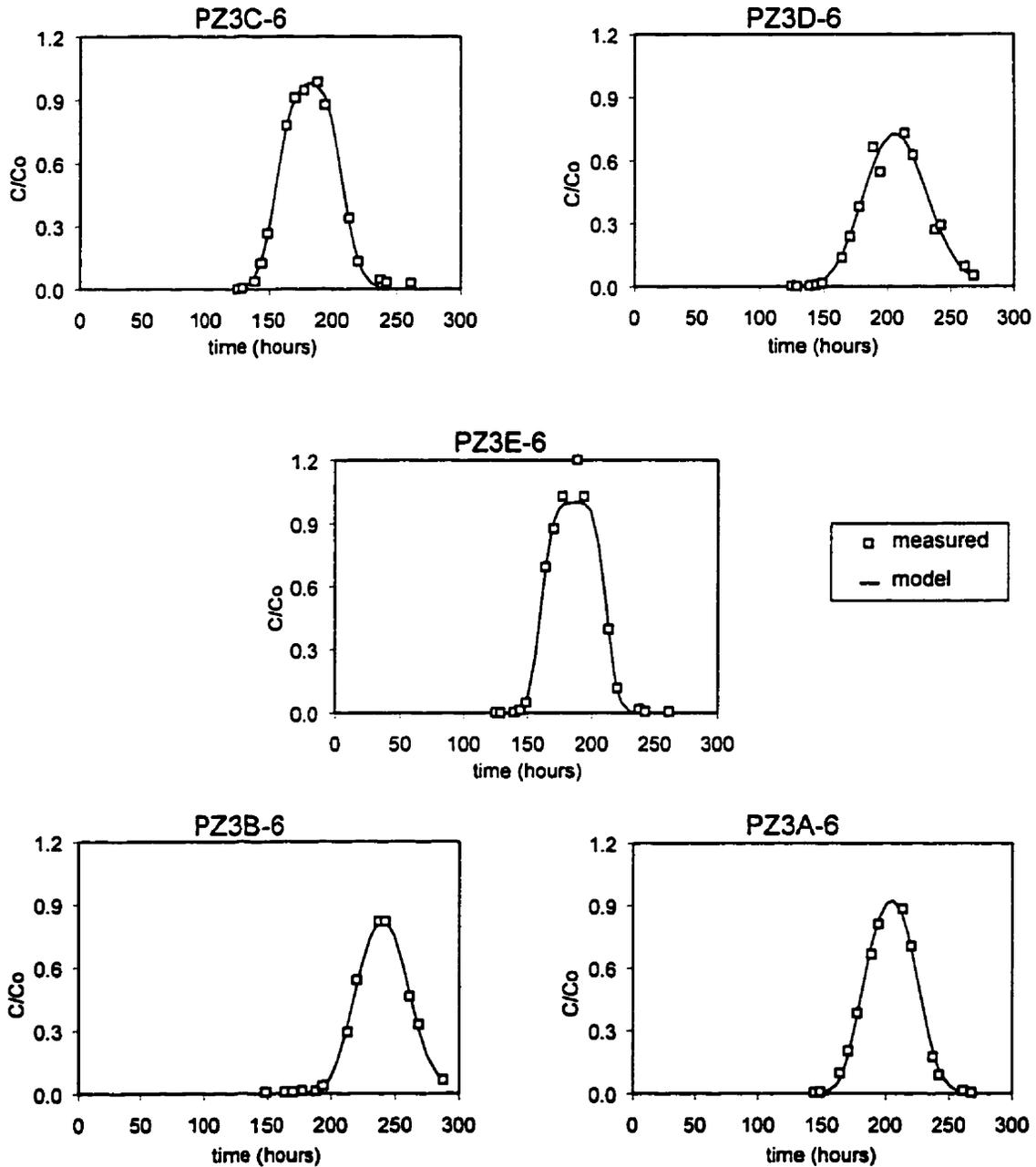


Figure B-8. Measured and calculated bromide breakthrough curves at 180-cm bgs ports in the Control Cell.

APPENDIX C. ANALYTICAL METHODS

C.1 Sampling Procedures and Analytical Methods - Laboratory Samples

Aromatic Hydrocarbons. Microcosm vials were decrimped and aliquots of liquid quickly transferred with a glass syringe to either 22-ml autosampler vials or 18-ml hypovials, which were then crimp sealed, and analyzed immediately. Samples were collected outside the anaerobic chamber. The pentane microextraction technique was used to quantify the aromatic hydrocarbons. The analytical methodology is described in the following section.

Dissolved Oxygen. In the laboratory, the dissolved O₂ concentration in microcosm liquid was determined immediately after organic sample collection. Measurements were typically made within 30 seconds of opening a microcosm, and care was taken to minimize the disturbance of the liquid. Dissolved O₂ determinations were made with either the azide-modified Winkler titration method (APHA, 1985), or a D.O. meter (Microelectrodes, Inc., Model MI-730), depending on the experiment. The analytical method was not changed within a given experiment.

For the Winkler method, 18-ml glass vials were flushed with argon, filled with microcosm liquid, and sealed with a Teflon™-lined septum and aluminum crimp seal. Winkler reagents were then injected directly into the vial using a syringe. The solution in the vial was then titrated with a standardized 0.0025 N sodium thiosulfate solution to determine the dissolved O₂ concentration. The MDL for this sample size was 0.05 mg/L. D.O. values determined with the Winkler method were corrected for the O₂ added to samples as a result of reagent addition. It was observed that the sodium azide used to inhibit microbial activity in control microcosms may have interfered with the analysis, resulting in D.O. concentrations that appeared to be anomalous. Consequently, the D.O. meter was used in the follow-up microcosm study (Experiment 3) to obtain data on initial dissolved O₂ concentrations and abiotic losses in the absence of microbial activity (i.e., sterile controls).

To obtain sample concentrations with the dissolved-O₂ meter a daily two-point calibration (0 to 21% dissolved O₂) was used. The instrument was zeroed with a 2% (w/v) sodium sulfite

solution. Measurements were made by inserting the probe directly into the microcosm liquid. To minimize diffusion of atmospheric O₂ into the sample, measurements were made under a stream of argon gas. Although steps were taken to minimize contamination with atmospheric O₂ during this sampling procedure, it could not be determined whether the low concentrations of dissolved O₂ that were typically observed after lengthy incubations in the anaerobic chamber (Chapter 4) resulted from positive sampling bias or were representative of microcosm liquid.

Nitrate and Nitrite. After collecting samples for organics and dissolved O₂, samples for NO₃⁻ and NO₂⁻ analysis were obtained by transferring an additional 15 ml of liquid to 18-ml plastic scintillation vials. These samples were preserved with 30 µL concentrated sulfuric acid and refrigerated until analysis. Nitrate and NO₂⁻ were determined colorimetrically with the automated cadmium reduction method, using a Technicon Autoanalyzer equipped with a 15 mm tubular flow cell and 550 nm filters. Before analysis, samples were diluted as required, and the pH adjusted with ammonium hydroxide to between 7 and 9. The MDLs were 0.2 mg/L and 0.26 mg/L for NO₂⁻ and NO₃⁻, respectively.

Nitrous Oxide. In microcosms that received acetylene, N₂O accumulation was measured using a GOW-MAC Series 350 GC equipped with a Thermal Conductivity Detector and a 6-ft, 100-120 mesh Poropak Q column. Samples were run isothermally at 40°C with a helium carrier (17 ml/min). Fifteen ml groundwater samples were collected from microcosms in 30 ml glass syringes. To obtain a gas-phase sample for analysis, syringes received 13-ml helium, and were sealed, shaken 100 times, and allowed to equilibrate for at least 2 hours. A sample loop was then used to inject a 2-ml gas sample onto the GC. Triplicate standards (0.1% and 0.5% N₂O in helium) were run to develop a two-point calibration curve. Partitioning theory was used to calculate the concentration of N₂O in the aqueous phase. The MDL was 0.45 mg/L dissolved N₂O. Acetylene was not quantified, but its presence was confirmed by reviewing chromatograms.

C.2 Analytical Methods - Field Samples

Aromatic Hydrocarbons. Concentrations of aromatic hydrocarbons in all groundwater samples collected in the field (as well as laboratory microcosms) were determined with a pentane micro-extraction procedure. Samples were first extracted by adding 1 ml of pentane containing

an internal standard (*m*-fluorotoluene) to 16.5 ml of groundwater and agitating for twenty minutes. Approximately 0.8 ml pentane was then transferred to an autosampler vial for analysis. Samples were run on an Hewlett Packard 5890 GC equipped with an HP7673A autosampler and a 30 m x 0.25 mm I.D. DB-5 column. The oven temperature program was 35°C for 1 min increasing to 165°C at 13°C/min with a 4 min final hold. The injector and detector temperatures were 200°C and 250°C, respectively. A calibration curve based on three standards was prepared for each sample run, and check standards were run approximately every ten samples. Standards were prepared by weighing known amounts of neat compounds into a known weight of methanol, and then diluting the stock solution into water to obtain a concentration range that bounded expected sample concentrations. Standards were analyzed in triplicate. Results for *m*-xylene and *p*-xylene were reported as a sum because these two compounds co-eluted on this column. The MDLs were 19 µg/L (benzene), 13 µg/L (toluene), 8 µg/L (ethylbenzene, and *o*-xylene), 9 µg/L (*m*+*p* xylene, 135-trimethylbenzene, and 124-trimethylbenzene), 6 µg/L (123-trimethylbenzene), and 120 µg/L (naphthalene).

Concentrations of aromatic hydrocarbons in core-extract samples were determined by a direct injection of the extractant onto the GC. Samples were run on an Hewlett Packard HP 5890 GC equipped with an HP7673A autosampler, and a 30 m x 0.25 mm I.D. DB-5 column. A 3 µL on-column injection of methanol was performed. The oven temperature program was as follows: 35°C for 5 min increasing to 150°C at 10°C/min with a 5 min final hold. The injector and detector temperatures were 200°C and 250°C, respectively. As for aqueous samples, a calibration curve based on three standards was prepared for each sample run, and check standards were run approximately every ten samples. Standards were prepared by weighing known amounts of neat compounds into a known weight of methanol. The standards were then further diluted in methanol to reach the appropriate concentration range, and analyzed in triplicate. The mass of aquifer material and methanol in each sample was used to express concentrations in mg/ml methanol on a wet-weight basis (mg/kg). The average method detection limits, which varied with methanol and sample mass, were as follows: 2.6 mg/kg for benzene, toluene, ethylbenzene, and *p*+*m*-xylene; 1.3 mg/kg for *o*-xylene and the trimethylbenzene isomers; and 3.9 mg/kg for naphthalene.

To measure the concentrations of aromatic hydrocarbons in API 91-01 gasoline, samples were prepared by weighing 15 ml of methanol into pre-weighed 40-ml glass vials with Teflon-

faced septa. Approximately 0.5 ml of gasoline were then weighed into the methanol and mixed. Aliquots were then transferred to autosampler vials for analysis. Standards were prepared as described in the previous paragraph. Concentrations were expressed as g analyte/g gasoline or weight percent.

Inorganic Parameters. Inorganic parameters were analyzed by the Water Quality Laboratory at the University of Waterloo. Anions such as SO_4^{2-} , Br^- , NO_3^- , and NO_2^- were analyzed using a Dionex System 2000 Ion Chromatograph equipped with a Dionex AS4A anion exchange column. A daily run of 20 to 50 samples contained 10 to 20 in-house standards. A commercially-prepared standard was run along with in-house standards to maintain standard quality. Samples were reanalyzed if the commercial standard did not come within five percent of its stated value. The method detection limit for all compounds was 0.05 mg/L.

Because the highly-contaminated water samples collected in this study appeared to be damaging the anion exchange column, most of the NO_3^- and NO_2^- samples collected after the first month of the flushing experiment were analyzed colorimetrically using the automated cadmium reduction method. Samples were run on an Alpkem Perstorp Analytical Environmental Flow Solution system. In-house standards were run for calibration and quality control as described above. The method detection limits were 0.4 mg/L (NO_3^-) and 0.2 mg/L (NO_2^-). To verify that these two analytical methods provided consistent results, several batches of NO_3^- samples were analyzed by both methods.

Iron was analyzed on a Varian Model 1475 Atomic Absorption Spectrophotometer. All samples are run in duplicate. As above, samples are run with in-house standards and a commercially-prepared standard. Commercial standard were analyzed every five samples to monitor instrument drift. The method detection limit was 0.05 mg/L.

Dissolved Methane. Water samples for CH_4 analysis were analyzed on a Hewlett Packard 5840A GC equipped with a flame ionization detector and 30 m megabore GS-Q column. Analyses were run isothermally at 100°C with a helium carrier gas (12 ml/min). The detector and injector temperatures were 200°C and 100°C, respectively. To prepare samples for analysis, 15-ml aliquots of groundwater were withdrawn from the sample bottle into a 30-ml glass syringe. An additional

13 ml of helium was added, and the syringe was shaken and allowed to equilibrate for 3 hr. A 5 ml sample of the gas phase was then injected via a 2-ml sample loop. The GC was calibrated in an external standard mode using several concentrations of a commercial gas mixture (Praxair). Henry's Law, the Ideal Gas Law and CH₄ solubility were then used to calculate concentrations in the aqueous phase. The MDL for dissolved CH₄ was 0.1 µg/L.

Metabolites. Descriptions of these analytical methods are provided elsewhere (Barcelona et al., 1995 (NCIBRD Laboratory); Hutchins et al., 1998 (NRMRL)).

APPENDIX D: AQUIFER MONITORING RESULTS

Table D-1. Environmental monitoring downgradient of wastewater treatment mound and treatment cells. All concentrations in mg/L.												
	Sample I.D.	Date	Depth (m bgs)	Ben	Tol	Eben	m+p-Xyl	o-Xyl	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB	Naph
Wastewater Treatment Mound												
	E-640	10/2/96	0.4 - 1.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	E-641	10/16/96	0.4 - 1.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	E-821	5/27/98	0.4 - 1.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bundle Piezometer												
	BP5-1	E-795	7/9/97	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BP5-1	E-822	5/27/98	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BP5-2	E-796	7/9/97	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BP5-2	E-823	5/27/98	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BP5-3	E-797	7/9/97	1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BP5-3	E-824	5/27/98	1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Treatment Cells												
Bundle Piezometers												
	BP1-1	E-635	10/2/96	2.9	0.010	n.d.	0.010	n.d.	n.d.	n.d.	n.d.	n.d.
	BP1-2	E-636	10/2/96	3.2	n.d.	n.d.	0.007	n.d.	n.d.	n.d.	n.d.	n.d.
	BP1-3	E-637	10/2/96	3.5	n.d.	n.d.	0.007	n.d.	n.d.	n.d.	n.d.	n.d.
	BP1-4	E-638	10/2/96	3.8	n.d.	n.d.	0.011	n.d.	n.d.	n.d.	n.d.	n.d.
	BP1-5	E-639	10/2/96	4.1	n.d.	n.d.	0.008	n.d.	n.d.	n.d.	n.d.	n.d.
	BP2-1	E-629	10/2/96	2.4	0.016	n.d.	0.015	n.d.	n.d.	n.d.	n.d.	n.d.
	BP2-2	E-630	10/2/96	2.7	0.012	n.d.	0.012	n.d.	n.d.	n.d.	n.d.	n.d.
	BP2-3	E-631	10/2/96	3.0	0.010	n.d.	0.011	n.d.	n.d.	n.d.	n.d.	n.d.
	BP2-4	E-632	10/2/96	3.3	0.013	0.016	0.05	0.016	0.013	0.046	0.013	0.074
	BP2-4	E-642	10/16/96	3.3	0.014	0.009	0.033	0.010	0.009	0.032	0.009	0.026
	BP2-5	E-633	10/2/96	3.6	0.014	0.010	0.030	0.010	0.015	0.053	0.014	0.027
	BP2-6	E-634	10/2/96	3.9	0.011	n.d.	0.011	n.d.	n.d.	n.d.	n.d.	n.d.
	BP3-4	E-371	7/2/96	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BP3-4	E-827	10/2/96	3.6	0.027	0.008	0.022	0.006	n.d.	n.d.	n.d.	n.d.
	BP3-4	E-793	7/9/97	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BP3-4	E-827	5/27/98	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table D-1. Environmental monitoring downgradient of wastewater treatment mound and treatment cells. All concentrations in mg/L.											
Sample I.D.	Date	Depth (m bgs)	Ben	Tol	Eben	m+p-Xyl	o-Xyl	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB	Naph
BP3-5 E-372	7/2/96	3.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP3-5 E-628	10/2/96	3.9	n.d.	0.024	0.007	0.019	n.d.	n.d.	n.d.	n.d.	n.d.
BP3-5 E-794	7/9/97	3.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP3-5 E-828	5/27/98	3.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP4-5 E-373	7/2/96	3.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP4-5 E-625	10/2/96	3.7	n.d.	0.06	0.015	0.039	0.013	n.d.	0.007	n.d.	n.d.
BP4-5 E-642	10/16/96	3.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP4-5 E-791	7/9/97	3.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP4-5 E-825	5/27/98	3.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP4-6 E-374	7/2/96	4.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP4-6 E-626	10/2/96	4.0	n.d.	0.026	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
BP4-6 E-792	7/9/97	4.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BP4-6 E828	5/27/98	4.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. - Not detected. Detection limits provided in Appendix C.

APPENDIX E: MASS-BALANCE CALCULATIONS

To simplify the mass-balance analysis, it was assumed that flow in the cells was at steady state under flushing conditions. The injection rate could then be used to estimate mass fluxes both into and out of the cells, as required. In addition the volumetric flow rates were assumed constant in space (i.e., the treatment cells were treated as one-dimensional columns), and time (i.e., mean injection rates were used in calculations). These assumptions were supported by the continuous injection and constant upper and lower head conditions maintained during the flushing experiments, as well as the Br⁻ tracer-test results. For all constituents, the mass advected across the horizontal plane located 20 cm above the top of the extraction well screen (180 cm bgs) was used as the most reliable measure of the mass "extracted" from the cells. For most of the mass-balance calculations, data from the extraction wells were not used because concentrations may have been affected somewhat by cyclical pumping rates and unquantified dilution with underlying groundwater.

E.1 Dissolved Oxygen

Because of the difficulties associated with obtaining reliable results from the multilevel piezometers, a rigorous mass balance was not performed on the dissolved O₂. However, the mass injected into each cell was estimated using a simple mass flux calculation. In this study, mass flux was calculated for the entire 2m x 2m area rather than a unit area; mass flux (QC) therefore had units of [M/T]. The mass injected into each cell was obtained by integrating the advective mass flux over the 174-day injection period:

$$M = \int_0^t F dt = \int_0^t Q(t)C(t) dt = \bar{Q}\bar{C}t \quad \text{E-1}$$

where \bar{Q} [L³/T] and \bar{C} [M/L³] are the mean volumetric injection rates and dissolved O₂

concentrations, respectively, t is the elapsed time, and M is the mass. The propagated error in this mass estimate was calculated from:

$$s_M^2 = M^2 \left(\frac{s_C^2}{C^2} + \frac{s_Q^2}{Q^2} \right) \quad \text{E-2}$$

where s_M^2 , s_C^2 , and s_Q^2 are the variances of the respective means (Bevington, 1969). Using the mean injection rates and dissolved O_2 concentrations provided in Sections 3.4.3 and 5.1.2, respectively, the masses of O_2 injected into the cells over the 174-day flushing experiment were 143 ± 115 g (Nitrate Cell) and 136 ± 100 g (Control Cell). To calculate the additional masses pumped into the cells during the 24-day flushing experiment, mean injection concentrations (4.6 ± 1.3 mg/L ($n=5$) and 4.5 ± 1.4 mg/L ($n=5$) for the Nitrate and Control Cells, respectively) were multiplied by the injection rate (200 ml/min, based on one measurement in each treatment cell), and the error was calculated from Equation E-2. Resulting masses of O_2 injected into the cells during this period were 32 ± 9 g (Nitrate Cell) and 31 ± 10 g (Control Cell).

Although the magnitude of the trapped air phase was not measured, it is possible to estimate the size of this O_2 reservoir. Assuming that the volumetric residual air content was in the range of 5-10% (pers. comm., R.W. Gillham), a dewatered volume of 4.4 m^3 ($2\text{m} \times 2\text{m} \times 1.1 \text{m}$ height), and an oxygen gas density of 1.43 g/L (standard temperature and pressure) (Hillel, 1982), the initial mass of O_2 could range from 60-120 g per cell. Based on the assumptions given above, the mass of O_2 derived from trapped air was roughly 50-100% of the mean injected O_2 masses, and therefore probably constituted a significant component of the total O_2 budget. Considering both sources of O_2 , the total mass available for reactions may have been as high as ca. 300 g per cell.

E.2 Nitrate

The NO_3^- mass loss during the 174-day flushing experiment was estimated by comparing the NO_3^- masses injected into and extracted from the Nitrate Cell. Data collected during the 24-day flushing period were insufficient to perform a mass balance, but qualitatively, the rate of NO_3^- utilization, as indicated by concentration differences, was similar. Mass loss was obtained by

difference from $M_{loss} = M_{injected} - M_{extracted}$. Injected and extracted masses were calculated by integrating the advective mass flux into and out of the cell, respectively, over the 174 day flushing experiment:

$$M = \int_0^t F dt - \int_0^t Q(t)C(t) dt - \bar{Q} \int_0^t C(t) dt \quad E-3$$

where,

- F = Mass flux [M/T],
- \bar{Q} = Mean injection rate [L³/T],
- C = NO₃⁻ concentration at time t [M/L³],
- t = Time [T]

Because the product QC (mass flux) was not available for every sampling event, masses were calculated using the mean injection rate (\bar{Q}) over the entire flushing period. The integral Cdt was evaluated numerically with a FORTRAN code adapted from Bevington (1969). To calculate the mass added to the cell, the injection NO₃⁻ concentration vs. time curve was integrated (Figure 5-6), and then multiplied by the mean injection rate. To calculate the mass advected across the 180 cm bgs plane (extracted mass), the NO₃⁻ BTCs from each of the ports at this depth were first integrated with respect to time, and then an unweighted mean value for this integral was obtained. This quantity was then multiplied by the mean injection rate to calculate the NO₃⁻ mass. Equation E-2 was used to calculate the propagated error in the mass estimate. As shown in Table 5-4, 7,130±390 g were pumped into the cell during the 174-day flushing experiment, and 6,240±1,160 g were removed. By difference, the calculated mass loss for this period was 890±1,220 g, where the propagated error, expressed as a standard deviation, was calculated from $s_{M_{loss}}^2 = s_{M_i}^2 + s_{M_e}^2$ (Bevington, 1969). The large error in the mass-loss estimate arises from the substantial spatial variability associated with the amount of mass flushed from the cell. During the following 24-day flushing experiment (mean injection concentration 116.4±10.2 mg/L (n=5)), an additional 802±70 g NO₃⁻ was pumped into the cell, for a total injected mass of approximately 7.9 kg NO₃⁻. Because of sparse data, the mass extracted from the cell during this period was not calculated, but

concentrations at the 180-cm depth were similar to those measured during the 174-day experiment.

5.2.3 BTEXTMB

The goal of this mass balance was to estimate the extent of aromatic-hydrocarbon mass loss in each treatment cell. BTEXTMB mass losses were calculated by comparing the initial mass of a constituent in the gasoline to the sum of the mass flushed by advection plus the mass remaining in the gasoline-contaminated zone. The sorbed mass was negligible relative to the other terms in the mass-balance equation, and therefore, was not explicitly considered here. Because it was not feasible to core the cells repeatedly, cores were not collected prior to the flushing experiment to determine the initial mass. This mass balance therefore represents total losses that were incurred over the entire 19-month period from the gasoline spill to final core collection. Volatilization losses were minimized by cell construction, but any losses by this mechanism would be included in the M_{LOSS} term. Total mass loss was obtained by difference,

$$M_{LOSS} = M_i - (M_a + M_r) \quad E-4$$

where,

M_{LOSS}	=	Mass loss over time period of interest,
M_i	=	Initial mass in gasoline,
M_a	=	Mass removed from flushing, and
M_r	=	Mass remaining in the gasoline-contaminated zone.

For a given constituent, the initial mass, M_i , in 70 liters of fresh gasoline was calculated from weight fraction of the constituent and the density of the gasoline (see Table A-2). As discussed in Appendix A, the weight-fraction data were found to be representative of the composition of fresh API 91-01. Initial masses are shown in Table 5-5. Relative to other components of the mass balance, the uncertainty in the initial mass was probably small.

Estimates of the mass flushed from the cells were obtained for both the 174-day and the following 24-day flushing experiments. These masses were then added to obtain total flushed mass, M_f , for each constituent (Table 5-5). To determine the mass advected across the 180-cm bgs plane during the 174-day experiment (extracted mass), the approach described above for NO_3^- was followed. It should be noted that data points were added to each of the piezometer BTCs to close some existing gaps. Because samples were not collected at 180 cm until Day 16, concentrations from this sampling event were extrapolated linearly to day 7. An additional data point was also added to Control-Cell BTCs; concentrations from day 155, the last sampling event in this cell, were extrapolated to day 174. These changes were supported by the tracer test, which showed sharp arrival of fronts at 180 cm within seven days, and the extraction-well BTCs, which confirmed that extrapolated concentrations were reasonable. To calculate the small additional mass removed during the 24-day pumping period, fewer data were available, and the simpler approach described in Section 5.2.1 for dissolved O_2 was followed. For each constituent, a mean concentration was calculated from extraction-well samples ($n=3$). This mean was then multiplied by the injection rate (200 ml/min) to obtain a mass estimate, and the error was again calculated from Equation E-2. Proportionally the largest errors were associated with benzene and toluene, which had large spatial variations in breakthrough behavior.

The mass remaining in the cells, M_r , was estimated from concentrations in core-extract samples. To obtain a mass estimate for the entire cell from discrete samples, an approach similar in principle to Freyberg (1986) was followed. As discussed in detail in Freyberg (1986), an estimate of the mass in a volume of interest can be obtained by integrating the concentration distribution:

$$M_r = \int_{x_1}^{x_2} \int_{y_1}^{y_2} C_i(x,y) \, dx \, dy \quad \text{E-5}$$

where C_z is obtained from

$$C_z = \int_{z_1}^{z_2} C(x,y,z) dz \quad \text{E-6}$$

The concentration, C_z , is expressed above in terms of mass per unit volume of porous medium. The limits of integration in Equation E-5 correspond to the cell dimensions (2 m by 2 m), and in Equation E-6 to the vertical length of the core.

The mass of each constituent was determined by first transforming concentrations in mg/kg to g/m^3 aquifer material using a wet bulk density of 2.15 g/cm^3 , calculated from the well-characterized dry bulk density of Borden sand of 1.82 g/cm^3 (Ball et al., 1990), and a fully-saturated porosity of 0.33 (Mackay et al., 1986). At each core location, concentration profiles (Figures 5-14 and 5-15) were then vertically integrated by multiplying each concentration by the appropriate depth interval, Δz , yielding an integrated concentration, C_z , in g/m^2 . Kriging was then used to interpolate vertically-integrated data from all of the core locations within a cell onto a regular grid. A linear model of the observed variogram was used to determine the weighting factors in the kriging matrix. Concentration contours of the kriged grid data agreed very well with hand-drawn contours based on linear interpolations between core locations. As an example of the kriged concentration distribution, a contour plot of vertically-averaged, total BTEXTMB concentrations in the Nitrate Cell is shown in Figure E-1. An areal integration of the kriged surface (concentration in $\text{g/m}^2 \times \text{area in m}^2$) was then performed to obtain the total mass of the constituent in grams. The GEOSOFT Mapping and Processing System (GeoSoft Inc., 1994) was used to calculate the variogram, kriging the concentration data, and integrate the kriged surface. Results are summarized in the second column of Table 5-5.

Several assumptions were made in arriving at these residual mass estimates. Because core recoveries were less than 100% of the core run, it was necessary to assign depth intervals to the recovered aquifer material. The calculations in Table 5-5 assume that compaction of the aquifer material inside the core barrel was minimal, and that, because of increasing frictional resistance

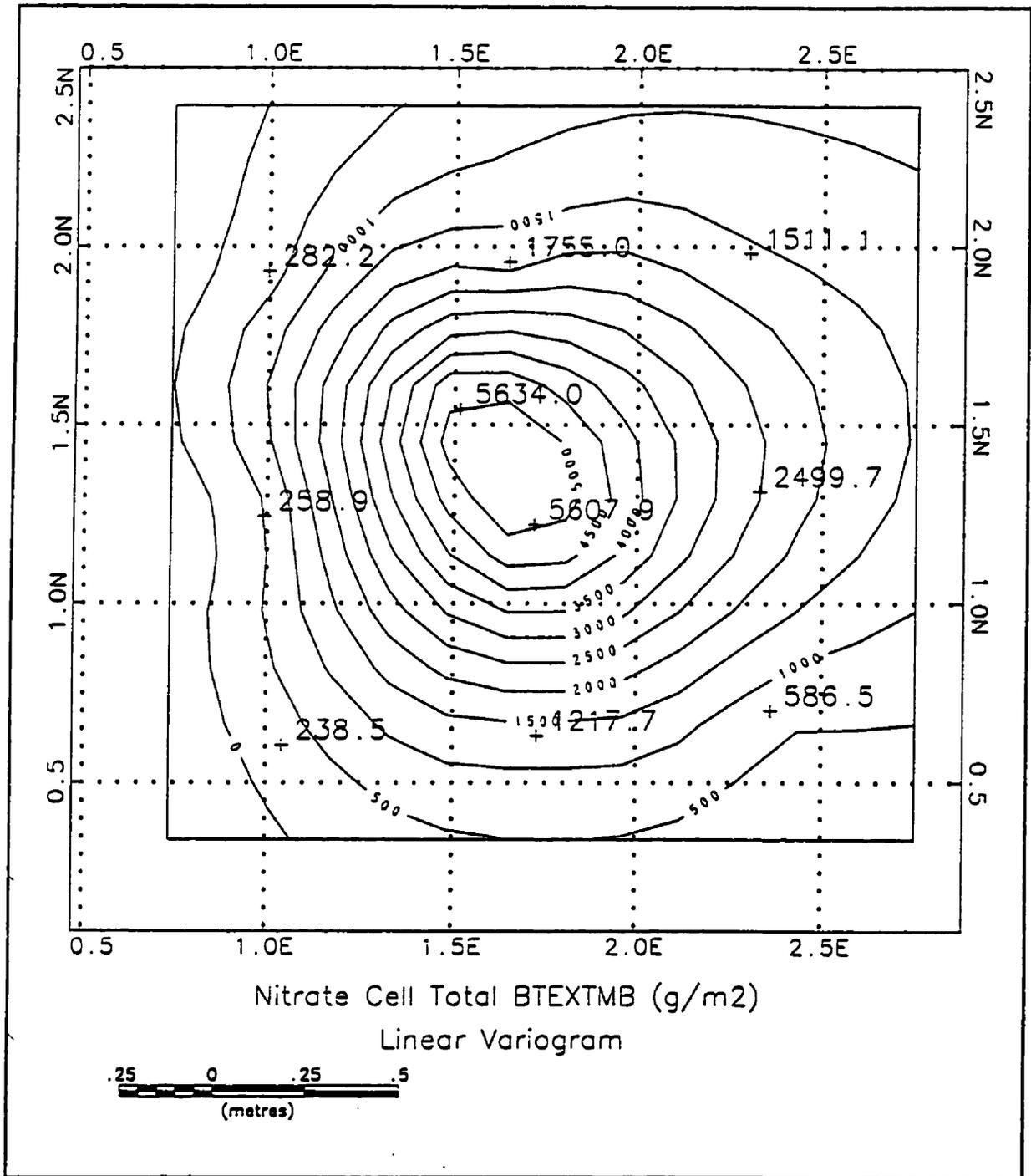


Figure E-1. Concentration contours for vertically-integrated total BTEXTMB concentrations in core extracts collected from the Nitrate Cell. Plot generated by GeoSoft as discussed in text.

inside the core barrel as the run proceeded, the missing interval was from the bottom of the core run. Consequently, a core from ground surface with 100 cm recovery was taken to represent the 0 to 100 cm depth interval. This conservative assumption may have imparted a negative bias on the residual mass estimates. Had the lack of complete recovery been attributed to uniform compaction along the core, the lengths of the contaminated intervals, and hence the mass estimates, would have increased by up to 20%. Although the Borden aquifer is comprised mainly of relatively-incompressible quartz sand, the material near the top of the cell was redistributed and fairly soft, and so compaction may have accounted for some of the apparent losses of material; there was, however, no clear way to determine the extent of compaction in these cores.

Second, the magnitude of the wet bulk density (2.15 g/cm^3) was calculated on the assumption that the sub-samples were fully saturated with water. On the basis of the rapid extraction and capping of the cores, and visual observations while coring, the assumption of full saturation appeared reasonable. Calculations were also simplified by treating the bulk density as a spatially-uniform parameter, and ignoring the small effect of residual gasoline on the magnitude of the bulk density. The value of the bulk density used here may also have resulted in a systematic overestimation or underestimation of the true mass in the aquifer samples.

The mass calculations also required assigning numerical values to the samples with concentrations below method detection limits. A sensitivity analysis showed that, with the exception of benzene and naphthalene, calculations were not sensitive to the value used for the detection limit; mass estimates varied by less than one percent when concentrations in not-detected samples were varied from zero to the value of the detection limit. For benzene and naphthalene, which had higher proportions of samples below detection limits, mass estimates increased by more than 10% when the detection-limit-value was used in the calculation. However, in the absence of a gasoline phase, the detection-limit value overestimated the total mass that would be present in the sorbed and aqueous phases. Because most of the samples were from locations that did not contain gasoline, concentrations of all constituents in samples below detection limits were assumed to be zero in the calculation of residual mass presented here. This may have resulted in a small underestimation of the residual mass. Finally, it was necessary to estimate the lengths of the contaminated intervals of the lowest samples in cores 4L and 3K. These cores did not straddle the contaminated zone, so the base of the lowest interval was undefined. In

both cells, the lengths were chosen to be consistent with adjacent cores, 4K and 3J, which had similar vertical concentration profiles (Figures 5-14 and 5-15).

These assumptions, losses arising from the coring and methanol-extraction procedure (Section 3.4.4), and the process of creating smooth concentration distributions from discrete data probably led to substantial error in the estimates of residual mass. It was not possible, however, to determine the magnitude of this uncertainty quantitatively. Accordingly, the error in the total amount of recovered mass is not given on Table 5-5, but based on error propagation considerations, its magnitude is at least as large as the uncertainty in the flushed mass.

APPENDIX F. TABULATED ANALYTICAL DATA

ORGANIC GEOCHEMISTRY LABORATORY
SUPPLEMENTARY QUALITY CONTROL/QUALITY ASSURANCE ANALYTICAL EVALUATION
FOR METHANOL SOIL EXTRACTION OF BTEX, TMB'S AND NAPHTHALENE
FOR: JEFF BARBARO

JAN 28, 1999 – SET UP
FEB 3, 1999 – SHAKING/MIXING
FEB 11, 1999 – GAS CHROMATOGRAPHIC ANALYSIS

CORE MATERIAL USED:

PRISTINE CORE: Used Borden core 2-2 from my grey fridge – used for INT test (Mario Shirmer – collected on June 12, 1997)

CONTAMINATED CORES: Used upper 1-2 ft of Borden cores 4M, 4O and 4R (Jeff Barbaro collected on Dec 16, 1997 and possibly 1 other date?)

SAMPLE PREPARATION PROCEDURE:

1. Weighed 40 ml VOA vials with Teflon screw cap lids (took special care to choose tight fitting caps)
2. Added 15 ml of methanol (without internal standard) and re-weighed the vials (weighed enough vials + methanol for the whole experiment – not more than 1 day ahead of time).
3. Quickly transferred (with a stainless steel spatula) approximately 10 g of the appropriate soil type to each of the vials (see list of sample plan under experimental design below).
4. Re-weighed the vials.
5. Spiked known amounts of API-91-01 gasoline into appropriate vials (200 ul –see Appendix A, and list of sample plan under experimental design below)
6. Vials were placed in the fridge (4C) for 7days
7. After 7 days incubation, vials were shaken on a rotary shaker for 15 min at > 250 rpm and sonicated for 3 min.
8. Vials were returned to the fridge (4C) for another 7days of incubation and then gas chromatographic analysis occurred.

GAS CHROMATOGRAPHIC ANALYTICAL PROCEDURE: (as modified from Jeff's thesis)

Concentrations of aromatic hydrocarbons in core-extract samples were determined by a direct injection of the methanol extractant onto the GC. Samples were run on an Hewlett Packard HP 5890 GC equipped with an HP7673A autosampler, and a 30 m x 0.25 mm I.D. DB-5 column (stationary phase thickness – 0.25 micron). A 2 ul on-column injection of methanol was performed. The oven temperature program was as follows: 35C for 5min increasing to 165C (at 13 degrees per min) and held for 10 min. A calibration curve based on three to five standards, was prepared. Standards were prepared by weighing known amounts of neat compounds into a known weight of methanol. The standards were then further diluted in methanol to reach the appropriate concentration range, and analyzed in triplicate. The mass of aquifer material and methanol in each sample was used to express concentrations in mg/Kg of methanol on a wet-weight basis (concentrations were then converted to mg/kg soil- not dry weight corrected). The average method detection limits, which varied with methanol and sample mass, were as follows: 2.2 mg/kg for benzene, toluene, ethylbenzene, and p+m xylene, o-xylene, trimethylbenzene isomers; and 3.9 mg/kg for naphthalene.

EXPERIMENTAL DESIGN:

Some standards were included during the sample incubation period, but they were not used to make the calibration curve (they were used to determine incubation/mixing losses). Fresh standards were prepared on the day of analysis and used to make the calibration curve. Gasoline standards were also prepared on the day of analysis and used to evaluate the recovery of gasoline from core samples.

SAMPLE LIST OF SAMPLES ANALYZED:

BLANK-1
PRISTINE-1
PRISTINE-2
PRISTINE-3
PRISTINE-4
PRISTINE-5
PRISTINE-6 PLUS GAS SPIKE
PRISTINE-7 PLUS GAS SPIKE
PRISTINE-8 PLUS GAS SPIKE
PRISTINE-9 PLUS GAS SPIKE
PRISTINE-10 PLUS GAS SPIKE
4M CONTAMINATED-1
4M CONTAMINATED-2
4M CONTAMINATED-3
4M CONTAMINATED-4
4M CONTAMINATED-5
4M CONTAMINATED-6 PLUS GAS SPIKE
4M CONTAMINATED-7 PLUS GAS SPIKE
4M CONTAMINATED-8 PLUS GAS SPIKE
4M CONTAMINATED-9 PLUS GAS SPIKE
4M CONTAMINATED-10 PLUS GAS SPIKE
BLANK-2
STANDARD-1 (3 ml of A standard)
STANDARD-2 (3 ml of A standard)
STANDARD-3 (500 ul of A standard)
STANDARD-4 (500 ul of A standard)
STANDARD-5 (250 ul of A standard)
STANDARD-6 (250 ul of A standard)
STANDARD-7 (200 ul of A standard)
STANDARD-8 (200 ul of A standard)
4O CONTAMINATED-1
4O CONTAMINATED-2
4O CONTAMINATED-3
4O CONTAMINATED-4
4O CONTAMINATED-5
4O CONTAMINATED-6 PLUS GAS SPIKE
4O CONTAMINATED-7 PLUS GAS SPIKE
4O CONTAMINATED-8 PLUS GAS SPIKE
4O CONTAMINATED-9 PLUS GAS SPIKE
4O CONTAMINATED-10 PLUS GAS SPIKE
4R CONTAMINATED-1
4R CONTAMINATED-2
4R CONTAMINATED-3
4R CONTAMINATED-4
4R CONTAMINATED-5
4R CONTAMINATED-6 PLUS GAS SPIKE
4R CONTAMINATED-7 PLUS GAS SPIKE
4R CONTAMINATED-8 PLUS GAS SPIKE
4R CONTAMINATED-9 PLUS GAS SPIKE
4R CONTAMINATED-10 PLUS GAS SPIKE
BLANK-3
GAS SPIKE -1
GAS SPIKE -2

GAS SPIKE -3
GAS SPIKE -4
GAS SPIKE -5

RESULTS: See attached spreadsheet

APPENDIX A

CALCULATION TO DETERMINE GASOLINE ADDITION TO SOIL MATRIX:

August 1998 – API 91-01 Gasoline – measured concentrations of aromatic hydrocarbons expressed in weight percent (from Jeff Barbaro's thesis)

Benzene	0.97
Toluene	8.21
Ethylbenzene	3.30
m+p xylene	7.60
o-xylene	2.59
1,3,5 TMB	1.11
1,2,4 TMB	2.97
1,2,3 TMB	0.69
Naphthalene	0.69

Add 200 ul of gasoline per 15 ml of methanol

Density of API 91-01 gasoline = 0.747g/ml

Density of Methanol = 0.79 g/ml

Weight of Gasoline = $0.2\text{ml} * 0.747\text{g/ml} = 0.1494\text{ g}$ added to $(15 * 0.79\text{g/ml})$ 11.85 g of methanol
= 12.61 g per Kg of methanol

For Benzene concentration = $0.0097 * 12.61\text{g} = 122.29\text{ mg/Kg}$ of methanol

For Toluene concentration = $0.0821 * 12.61\text{g} = 1035.28\text{ mg/kg}$ of methanol

APPENDIX B

Conversion of concentration of mg/Kg of methanol to mg/kg of soil:

Example: $\text{mg/Kg methanol} = \text{concentration of sample from the standard curve} * \text{weight of methanol in the vial} = \text{mg} * \text{weight (approximately 10g) of soil in the vial} = \text{mg/kg of soil}$

50000001

SAMPLES - METHANOL EXTRACTION OF SOIL 11-Feb-99
 Lab Number 890214
 All samples prepared on Jan 28, 1989 (unless otherwise stated)
 Jeff Barbaro

n	sample		pristine / pristine +gasoline spike (mg/kg soil)		%recovery		gas spike added		recovered		%recovery		n
	avg	%rsd	avg	%rsd	avg	%rsd	avg	%rsd	avg	%rsd	avg	%rsd	
5	0.000	0.00	310.68	6.49	282.309	12.52	90.87	279.14	10.96	261.006	4.94	91.72	5
5	0.000	0.00	1055.38	6.49	928.379	14.62	87.97	948.22	10.96	875.531	4.51	87.90	5
5	0.000	0.00	543.33	6.49	483.492	15.03	88.99	488.17	10.96	484.050	4.42	88.83	5
5	0.000	0.00	1073.98	6.49	969.406	15.15	90.26	964.93	10.96	989.882	4.30	90.26	5
5	0.000	0.00	376.99	6.49	348.800	15.32	92.52	338.71	10.96	365.539	4.33	93.14	5
5	0.000	0.00	152.88	6.49	154.839	15.19	101.28	137.36	10.96	178.838	4.55	101.60	5
5	0.000	0.00	424.15	6.49	420.291	15.74	99.09	381.09	10.96	498.545	4.23	100.26	5
5	0.000	0.00	100.28	6.49	102.902	14.75	102.61	90.10	10.96	126.740	4.06	103.60	5
5	0.000	0.00	106.54	6.49	113.581	14.17	106.61	95.72	10.96	162.461	3.52	113.49	5

n	sample		40 / 40 + gasoline spike (mg/kg soil)		%recovery		gas spike added		recovered		%recovery		n
	avg	%rsd	avg	%rsd	avg	%rsd	avg	%rsd	avg	%rsd	avg	%rsd	
5	15.404	33.07	300.61	2.62	270.376	4.31	85.56	289.69	8.22	229.926	17.99	79.37	5
5	177.908	29.82	1021.17	2.62	977.518	4.80	81.52	984.07	8.22	804.388	8.98	81.74	5
5	187.874	21.28	525.72	2.62	575.107	6.65	80.59	508.02	8.22	424.812	7.89	83.85	5
5	403.191	20.11	1039.17	2.62	1177.082	6.62	81.61	1001.41	8.22	855.398	7.48	85.35	5
5	160.847	18.60	384.77	2.62	439.382	6.22	83.59	351.52	8.22	309.770	7.28	88.12	5
5	101.397	12.23	147.92	2.62	225.294	5.34	90.36	142.55	8.22	138.806	7.19	97.37	5
5	287.417	10.39	410.41	2.62	594.831	14.43	85.24	395.50	8.22	378.069	6.87	95.44	5
5	74.789	9.54	97.03	2.62	161.701	3.87	94.11	93.51	8.22	93.478	6.65	99.97	5
5	100.814	5.67	103.08	2.62	214.949	3.60	105.42	99.34	8.22	108.835	6.20	108.28	5

* means sample was resampled (from 15 ml of Methanol) on Feb 15, 1989 and then analyzed

SAMPLES - METHANOL EXTRACTION OF SOIL
 11-Feb-99
 All samples prepared on Jan 28, 1999 (unless otherwise stated)
 Jeff Barbaro

	A sid 3ml* (mg/kg MeOH)				A sid 0.5ml* (mg/kg MeOH)				n
	avg	%rsd	recovered	%rec	avg	%rsd	recovered	%rec	
benzene	1827.83	1.09	1835.376	100.41	287.48	1.32	321.344	111.78	2
toluene	1775.78	1.09	1761.297	99.18	279.30	1.32	313.225	112.15	2
ethylbenzene	1832.37	1.09	1802.284	98.36	288.20	1.32	321.648	111.61	2
p,m-xylene	3575.11	1.09	3518.165	98.41	562.30	1.32	628.076	111.70	2
o-xylene	1828.07	1.09	1795.154	98.15	287.68	1.32	318.600	110.75	2
1,3,5-trimethylbenzene	1768.52	1.09	1746.625	97.77	280.99	1.32	310.731	110.59	2
1,2,4-trimethylbenzene	1833.61	1.09	1793.436	97.81	289.39	1.32	318.322	110.38	2
1,2,3-trimethylbenzene	1841.46	1.09	1799.919	97.74	289.63	1.32	318.800	110.07	2
naphthalene	1719.19	1.09	1687.277	98.14	270.40	1.32	289.570	107.09	2

	A sid 0.25ml* (mg/kg MeOH)				B sid 0.2ml* (mg/kg MeOH)				n
	avg	%rsd	recovered	%rec	avg	%rsd	recovered	%rec	
benzene	158.32	14.55	160.558	0.77	13.02	0.19	14.640	1.67	2
toluene	153.81	14.55	155.630	1.16	13.00	0.19	15.105	1.35	2
ethylbenzene	158.71	14.55	159.833	1.27	12.60	0.19	14.776	1.40	2
p,m-xylene	309.65	14.55	312.335	1.67	25.42	0.19	29.583	1.68	2
o-xylene	158.42	14.55	157.511	2.08	13.22	0.19	15.139	1.73	2
1,3,5-trimethylbenzene	154.74	14.55	154.115	2.18	12.95	0.19	14.329	4.79	2
1,2,4-trimethylbenzene	158.82	14.55	157.185	2.15	13.20	0.19	14.432	2.37	2
1,2,3-trimethylbenzene	159.50	14.55	157.166	2.85	13.70	0.19	15.357	1.32	2
naphthalene	148.91	14.55	139.681	3.16	13.58	0.19	12.634	5.97	2

SAMPLES - mg/l	gas spike* (mg/kg MeOH)				blanks (mg/kg MeOH)			
	avg	%rsd	recovered	%rec	avg	%rsd	recovered	%rec
benzene	278.82	1.88	279.136	3.58	23.36	2.90	3	0.00
toluene	947.14	1.88	957.489	5.58	79.38	3.88	3	0.00
ethylbenzene	487.61	1.88	495.619	6.84	40.85	5.04	3	0.00
p,m-xylene	983.83	1.88	980.570	6.79	80.75	4.84	3	0.00
o-xylene	338.33	1.88	345.087	6.74	28.35	4.59	3	0.00
1,3,5-trimethylbenzene	137.20	1.88	140.558	6.88	11.50	4.23	3	0.00
1,2,4-trimethylbenzene	380.65	1.88	382.428	6.85	31.89	4.27	3	0.00
1,2,3-trimethylbenzene	90.00	1.88	94.022	6.43	7.54	4.24	3	0.00
naphthalene	95.61	1.88	100.885	7.63	8.01	3.51	3	0.00

* means sample was resampled (from 15 ml of Methanol) on Feb 15, 1999 and then analyzed

METHANOL EXTRACTION OF SOIL
Lab Number 990214

11-Feb-99

Jeff Barbaro

Standards prepared Feb 11, 1999

QA/QC DATA

CALIBRATION CURVE

Calibration Standard - (mg/Kg Meoh)

	Xo	N	X	%RSD	%E	Xo	N	X	%RSD	%E
benzene	286.261	4	286.411	4.044	0.05	139.969	4	138.209	4.123	-1.26
toluene	278.110	4	279.155	4.106	0.38	139.700	4	139.899	5.105	0.14
ethylbenzene	286.973	4	286.269	4.792	-0.25	135.385	4	136.126	6.405	0.55
p,m-xylene	559.907	4	559.097	5.125	-0.14	273.197	4	273.802	6.386	0.22
o-xylene	286.455	4	284.162	5.445	-0.80	142.127	4	140.613	6.609	-1.07
1,3,5-trimethylbenzene	279.792	4	277.541	5.784	-0.80	139.160	4	138.712	7.347	-0.32
1,2,4-trimethylbenzene	287.167	4	284.263	5.910	-1.01	141.857	4	139.527	7.598	-1.64
1,2,3-trimethylbenzene	288.396	4	285.627	6.089	-0.96	147.251	4	145.338	7.839	-1.30
naphthalene	269.247	4	257.838	7.127	-4.24	145.903	4	138.443	8.644	-5.11

Calibration Standard - (mg/Kg Meoh)

	Xo	N	X	%RSD	%E	Xo	N	X	%RSD	%E	-MDL
benzene	13.335	4	13.371	3.659	0.27	3.272	4	3.283	3.750	0.33	1.5
toluene	13.310	4	13.956	3.615	4.86	3.627	4	3.705	4.444	2.16	2.1
ethylbenzene	12.898	4	13.717	7.227	6.35	3.588	4	3.470	2.824	-3.26	2.0
p,m-xylene	26.028	4	27.903	7.207	7.20	6.544	4	7.420	3.498	13.39	2.7
o-xylene	13.541	4	14.096	7.585	4.10	3.745	4	3.967	2.858	5.92	2.1
1,3,5-trimethylbenzene	13.258	4	13.568	8.752	2.34	3.706	4	3.506	3.664	-5.38	1.4
1,2,4-trimethylbenzene	13.515	4	13.317	9.495	-1.47	3.351	4	3.269	4.017	-2.45	2.1
1,2,3-trimethylbenzene	14.029	4	14.152	9.861	0.88	3.785	4	3.741	7.842	-1.14	1.5
naphthalene	13.900	4	10.702	13.260	-23.01	5.362	4	3.209	20.352	-40.14	2.2

Calibration Standard - (mg/Kg Meoh)

	Xo	N	X	%RSD	%E
benzene	2.189	4	2.278	3.392	4.04
toluene	2.427	4	2.506	4.827	3.29
ethylbenzene	2.400	6	2.697	24.551	12.36
p,m-xylene	4.378	4	4.961	5.080	13.30
o-xylene	2.506	4	2.511	9.608	0.20
1,3,5-trimethylbenzene	2.479	4	2.193	9.527	-11.54
1,2,4-trimethylbenzene	2.242	4	2.231	4.741	-0.51
1,2,3-trimethylbenzene	2.532	4	2.417	7.412	-4.55
naphthalene	3.587	4	0.000	0.000	-100.00

Where :

Xo = true concentration of standard

N = number of replicates

X = calculated concentration of standard using regression curve

%RSD = percent relative standard deviation

%E = percent error of calculated value from the true value

U.S. EPA Denitrification Study											
Microcosm Experiment 1 - High concentration vs low BTEX/TMB concentration under mixed electron acceptor conditions.											
All concentrations in mg/L											
	Day 0	Day 42	Day 137		Day 0	Day 42	Day 137		Day 0	Day 42	Day 137
benzene				toluene				ethylbenzene			
High Conc.	11.267	16.737	17.853	High Conc.	19.386	32.973	31.722	High Conc.	3.052	5.425	4.912
	13.434	17.706	17.296		22.937	34.006	30.744		3.614	5.360	4.719
	14.289	17.149	17.762		24.793	32.922	31.780		3.993	5.295	4.919
	11.034	17.276	18.174		19.125	32.527	32.215		3.004	5.156	5.036
	14.530	17.126	17.209		25.206	31.927	30.896		4.037	5.050	4.184
	13.212	17.484	18.399		22.815	32.376	32.840		3.657	3.792	4.610
	13.605	17.925	17.579		22.903	33.193	31.021		3.639	5.398	4.850
mean	13.100	17.307	17.655	mean	22.559	32.882	31.521	mean	3.701	5.170	4.767
std dev.	1.267	0.379	0.466	std dev.	2.228	0.631	0.746	std dev.	3.587	5.081	4.750
C/Co	1.000	1.321	1.348	C/Co	1.000	1.458	1.397	C/Co	1.000	1.416	1.324
s.d. C/Co	0.139	0.133	0.137		0.140	0.147	0.142		0.150	0.212	0.159
Low Conc.	1.036	1.190	1.732	Low Conc.	1.894	0.179	0.888	Low Conc.	0.285	0.000	0.131
	1.089	1.131	1.497		1.901	0.203	0.189		0.288	0.000	0.011
	1.019	1.225	1.306		1.878	0.206	0.142		0.290	0.000	0.008
	1.051	1.255	1.120		1.929	0.247	0.136		0.296	0.000	0.008
	1.052	1.302	1.141		1.930	0.139	0.120		0.295	0.000	0.017
	1.068	1.274	1.316		1.929	0.204	0.100		0.294	0.069	0.008
	1.091	1.317	1.440		2.035	0.175	0.140		0.314	0.000	0.013
	1.038	1.198	1.245		1.888	0.173	0.119		0.287	0.000	0.010
mean	1.056	1.229	1.350	mean	1.923	0.191	0.227	mean	0.284	0.009	0.028
std dev.	0.028	0.071	0.202	std dev.	0.050	0.032	0.266	std dev.	0.009	0.024	0.043
C/Co	1.000	1.164	1.279	C/Co	1.000	0.099	0.118	C/Co	1.000	0.029	0.088
s.d. C/Co	0.034	0.073	0.184		0.036	0.017	0.139		0.044	0.083	0.145
Control	1.129	1.822	1.446	Control	1.971	2.924	0.976	Control	0.292	0.110	0.241
	1.075	1.810	1.732		1.946	2.883	2.498		0.282	0.103	0.061
	1.081	1.893	1.753		1.986	3.077	2.611		0.301	0.130	0.067
	1.144	1.637	1.675		2.005	2.471	2.265		0.305	0.000	0.040
	1.100	1.743	1.663		1.952	3.083	2.387		0.286	0.106	0.046
	1.093	1.557	1.639		1.985	2.901	2.661		0.308	0.066	0.090
	1.178	1.663	1.717		2.060	2.722	2.833		0.310	0.062	0.092
	1.124	1.613	1.619		1.971	2.933	2.211		0.284	0.092	0.045
mean	1.115	1.642	1.656	mean	1.995	2.876	2.305	mean	0.300	0.086	0.085
std dev.	0.034	0.057	0.098	std dev.	0.036	0.201	0.576	std dev.	0.007	0.040	0.066
C/Co	1.000	1.473	1.484	C/Co	1.000	1.449	1.162	C/Co	1.000	0.288	0.285
s.d. C/Co	0.044	0.069	0.088		0.026	0.104	0.291		0.033	0.134	0.220

NOTE: Detection limit for all organics approximately 100 ppb on day 42.
Nitrite detection limit = 0.2 mg/L; D.O. detection limit 0.05 mg/L

U.S. EPA Den Microchem E All concentrat	m-p-xylene		o-xylene		135-imb		Day 0	Day 42	Day 137	Day 0	Day 42	Day 137	Day 0	Day 42	Day 137
	Day 0	Day 42	Day 0	Day 42	Day 0	Day 42									
	6.164	11.018	2.990	5.432	2.990	5.432	0.335	0.577	0.497				0.335	0.577	0.497
	7.267	10.938	3.558	5.343	3.558	5.343	0.387	0.563	0.486				0.387	0.563	0.486
	8.129	10.769	3.952	5.291	3.952	5.291	0.421	0.547	0.514				0.421	0.547	0.514
	6.129	10.471	2.988	5.090	2.988	5.090	0.325	0.539	0.515				0.325	0.539	0.515
	8.227	10.193	4.020	5.033	4.020	5.033	0.432	0.527	0.493				0.432	0.527	0.493
	7.455	10.395	3.607	5.150	3.607	5.150	0.385	0.543	0.528				0.385	0.543	0.528
	7.403	10.943	3.612	5.444	3.612	5.444	0.391	0.580	0.466				0.391	0.580	0.466
	7.551	10.444	3.682	5.135	3.682	5.135	0.388	0.532	0.481				0.388	0.532	0.481
	7.293	10.634	3.551	5.240	3.551	5.240	0.383	0.549	0.501				0.383	0.549	0.501
	0.784	0.287	0.385	0.159	0.385	0.159	0.037	0.017	0.016				0.037	0.017	0.016
	1.000	1.458	1.000	1.476	1.000	1.476	1.000	1.432	1.309				1.000	1.432	1.309
	0.152	0.162	0.153	0.166	0.153	0.166	0.137	0.146	0.134				0.137	0.146	0.134
	0.591	0.174	0.287	0.366	0.287	0.366	0.040	0.000	0.055				0.040	0.000	0.055
	0.591	0.150	0.287	0.314	0.287	0.314	0.040	0.000	0.045				0.040	0.000	0.045
	0.591	0.191	0.287	0.388	0.287	0.388	0.040	0.000	0.047				0.040	0.000	0.047
	0.604	0.181	0.285	0.396	0.285	0.396	0.040	0.000	0.043				0.040	0.000	0.043
	0.600	0.177	0.293	0.377	0.293	0.377	0.041	0.000	0.043				0.041	0.000	0.043
	0.598	0.195	0.294	0.380	0.294	0.380	0.043	0.000	0.046				0.043	0.000	0.046
	0.647	0.202	0.314	0.378	0.314	0.378	0.045	0.000	0.047				0.045	0.000	0.047
	0.595	0.175	0.289	0.381	0.289	0.381	0.045	0.000	0.045				0.045	0.000	0.045
	0.601	0.191	0.293	0.375	0.293	0.375	0.041	0.000	0.046				0.041	0.000	0.046
	0.020	0.016	0.009	0.025	0.009	0.025	0.002	0.000	0.004				0.002	0.000	0.004
	1.000	0.301	1.000	1.278	1.000	1.278	1.000	0.000	0.004				1.000	0.000	0.004
	0.046	0.028	0.043	0.095	0.043	0.095	0.069	#DIV/0!	0.108				0.069	#DIV/0!	0.108
	0.606	0.923	0.298	0.469	0.298	0.469	0.009	0.000	0.072				0.009	0.000	0.072
	0.608	0.916	0.299	0.465	0.299	0.465	0.042	0.000	0.045				0.042	0.000	0.045
	0.824	0.975	0.302	0.480	0.302	0.480	0.042	0.000	0.048				0.042	0.000	0.048
	0.628	0.945	0.304	0.484	0.304	0.484	0.044	0.000	0.047				0.044	0.000	0.047
	0.610	0.994	0.296	0.497	0.296	0.497	0.041	0.000	0.048				0.041	0.000	0.048
	0.623	0.999	0.303	0.501	0.303	0.501	0.043	0.000	0.045				0.043	0.000	0.045
	0.645	0.971	0.314	0.492	0.314	0.492	0.009	0.000	0.048				0.009	0.000	0.048
	0.613	0.932	0.301	0.473	0.301	0.473	0.039	0.000	0.045				0.039	0.000	0.045
	0.620	0.957	0.302	0.484	0.302	0.484	0.034	0.000	0.050				0.034	0.000	0.050
	0.013	0.032	0.005	0.013	0.005	0.013	0.015	0.000	0.009				0.015	0.000	0.009
	1.000	1.544	1.000	1.602	1.000	1.602	1.000	0.000	1.472				1.000	0.000	1.472
	0.030	0.061	0.028	0.053	0.028	0.053	0.642	#DIV/0!	0.722				0.642	#DIV/0!	0.722

NOTE: Detect
Nitrite

U.S. EPA Designation	Microcosm E	All concentrations	Day 0	Day 42	Day 137	Day 0	Day 42	Day 137	naphthalene	Day 0	Day 42	Day 137
124-4mb												
High Conc.	1.068	1.872	1.669			0.316	0.602	0.523	High Conc.	0.553	1.225	0.929
	1.242	1.820	1.633			0.372	0.580	0.514		0.634	1.013	0.929
	1.373	1.777	1.710			0.412	0.583	0.540		0.697	1.062	0.908
	1.032	1.755	1.728			0.311	0.569	0.543		0.533	1.025	0.866
	1.399	1.723	1.650			0.424	0.546	0.522		0.717	1.018	0.863
	1.256	1.740	1.764			0.376	0.564	0.553		0.643	1.186	0.900
	1.264	1.837	1.689			0.369	0.592	0.523		0.648	1.082	0.862
mean	1.273	1.701	1.618			0.380	0.553	0.507		0.659	0.988	0.895
std dev.	1.238	1.778	1.680			0.370	0.574	0.528	mean	0.635	1.078	0.897
C/Co	0.130	0.060	0.050			0.040	0.019	0.016	std dev.	0.064	0.085	0.026
	1.000	1.436	1.357			1.000	1.550	1.427	C/Co	1.000	1.694	1.411
	0.146	0.158	0.148			0.153	0.176	0.160		0.142	0.216	0.147
Low Conc.	0.097	0.000	0.045			0.030	0.000	0.062	Low Conc.	0.039	0.000	0.076
	0.101	0.000	0.008			0.028	0.000	0.049		0.047	0.000	0.017
	0.104	0.000	0.008			0.030	0.000	0.053		0.060	0.000	0.088
	0.104	0.000	0.000			0.032	0.000	0.044		0.062	0.000	0.113
	0.098	0.000	0.000			0.032	0.000	0.045		0.064	0.000	0.068
	0.102	0.000	0.000			0.006	0.000	0.048		0.063	0.000	0.147
	0.109	0.000	0.015			0.032	0.000	0.048		0.042	0.000	0.118
	0.099	0.000	0.005			0.028	0.000	0.049		0.062	0.000	0.060
mean	0.102	0.000	0.010			0.027	0.000	0.050	mean	0.055	0.000	0.087
std dev.	0.004	0.000	0.015			0.009	0.000	0.008	std dev.	0.010	0.000	0.041
C/Co	1.000	0.000	0.097			1.000	0.000	1.834	C/Co	1.000	0.000	1.583
	0.064	#DIV/0!	0.148			0.457	#DIV/0!	0.629		0.266	#DIV/0!	0.799
Control	0.107	0.134	0.161			0.006	0.000	0.050	Control	0.120	0.000	0.092
	0.106	0.134	0.151			0.032	0.000	0.049		0.072	0.000	0.225
	0.103	0.143	0.159			0.032	0.000	0.053		0.042	0.000	0.136
	0.106	0.164	0.159			0.033	0.000	0.049		0.063	0.000	0.180
	0.101	0.142	0.151			0.030	0.000	0.051		0.065	0.000	0.197
	0.109	0.153	0.149			0.033	0.000	0.050		0.062	0.000	0.118
	0.115	0.139	0.160			0.006	0.000	0.052		0.120	0.000	0.135
	0.106	0.136	0.150			0.030	0.000	0.063		0.018	0.000	0.097
mean	0.107	0.143	0.155			0.025	0.000	0.052	mean	0.070	0.000	0.148
std dev.	0.004	0.010	0.005			0.012	0.000	0.005	std dev.	0.035	0.000	0.048
C/Co	1.000	1.342	1.454			1.000	0.000	2.064	C/Co	1.000	0.000	2.100
	0.055	0.111	0.075			0.669	#DIV/0!	0.993		0.707	#DIV/0!	1.254

NOTE: Deleted Nitrite

U.S. EPA Design Microcosm Experiment													
All concentrations													
	total btextmb				nitrate				nitrite				
		Day 0	Day 42	Day 137		Day 0	Day 42	Day 137		Day 0	Day 42	Day 137	
	High Conc.	45.131	75.861	72.938	High Conc.	100.280	104.540	92.900	High Conc.	0.200	0.200	0.200	
		53.465	77.229	70.677		103.050	95.360	102.200		0.200	0.200	0.200	
		58.069	75.295	72.900		104.460	93.120	100.590		0.200	0.200	0.200	
		44.481	74.408	74.348		100.280	93.120	99.010		0.200	0.200	0.200	
		58.992	73.145	70.470		105.900	95.360	107.140		0.200	0.200	0.200	
		53.406	73.210	75.138		101.650	94.240	103.820		0.200	0.200	0.200	
		53.649	76.117	71.059		100.280	97.620	97.450		0.200	0.200	0.200	
		54.547	75.691	71.197		96.250	114.080	103.820		0.200	0.200	0.200	
	mean	52.718	75.120	72.341	mean	101.519	98.430	100.866	mean	0.200	0.200	0.200	
	std dev.	5.327	1.434	1.762	std dev.	2.990	7.326	4.428	std dev.	0.000	0.000	0.000	
	C/Co	1.000	1.425	1.372	C/Co	1.000	0.970	0.994	C/Co	1.000	1.000	1.000	
		0.143	0.147	0.143		0.042	0.078	0.053		0.000	0.000	0.000	
	Low Conc.	4.299	1.929	3.898	Low Conc.	101.650	84.350	74.830	Low Conc.	0.200	0.200	0.200	
		4.370	1.798	2.379		107.360	86.700	69.720		0.200	0.200	0.200	
		4.299	2.011	2.272		100.280	94.240	69.720		0.200	0.200	0.200	
		4.413	2.079	1.974		96.250	87.610	74.830		0.200	0.200	0.200	
		4.405	1.995	1.968		97.580	80.080	74.830		0.200	0.200	0.200	
		4.395	2.122	2.189		97.580	84.350	70.990		0.200	0.200	0.200	
		4.629	2.070	2.387		98.920	93.120	76.140		0.200	0.200	0.200	
		4.318	1.865	2.098		100.280	80.080	76.140		0.200	0.200	0.200	
	mean	4.391	1.984	2.395	mean	99.988	86.566	73.400	mean	0.200	0.200	0.200	
	std dev.	0.107	0.112	0.629	std dev.	3.464	5.365	2.779	std dev.	0.000	0.000	0.000	
	C/Co	1.000	0.452	0.546	C/Co	1.000	0.866	0.734	C/Co	1.000	1.000	1.000	
		0.035	0.028	0.144		0.049	0.061	0.036		0.000	0.000	0.000	
	Control	4.538	6.182	4.755	Control	96.250	90.900	99.010	Control	0.200	0.200	0.200	
		4.472	6.111	6.141		96.250	90.900	99.010		0.200	0.200	0.200	
		4.513	6.508	6.278		97.580	109.260	103.820		0.200	0.200	0.200	
		4.632	5.701	5.957		101.650	98.760	107.140		0.200	0.200	0.200	
		4.491	6.575	5.930		101.650	114.080	105.470		0.200	0.200	0.200	
		4.557	6.197	6.116		104.460	109.260	110.570		0.200	0.200	0.200	
		4.755	6.049	6.480		100.280	106.890	114.110		0.200	0.200	0.200	
		4.496	6.179	5.605		103.050	109.260	114.110		0.200	0.200	0.200	
	mean	4.557	6.188	5.908	mean	100.146	103.664	106.655	mean	0.200	0.200	0.200	
	std dev.	0.094	0.271	0.532	std dev.	3.129	8.966	6.012	std dev.	0.000	0.000	0.000	
	C/Co	1.000	1.358	1.296	C/Co	1.000	1.035	1.065	C/Co	1.000	1.000	1.000	
		0.029	0.066	0.120		0.044	0.095	0.069		0.000	0.000	0.000	
NOTE: Detect Nitrite													

U.S. EPA denitrification Study													
Microcosm Experiment 2- High concentration BTEX under aerobic, aerobic plus nitrate, and killed control conditions													
All concentrations mg/L													
benzene	Day 1	Day 42	Day 73	Day 163	toluene	Day 1	Day 42	Day 73	Day 163	ethylbenzene	Day 1	Day 42	
	Act NO3	12.941	12.212	0.269		8.587	Act NO3	25.611	19.900		0.183	17.210	Act NO3
	12.668	9.254	3.323	0.052		25.398	18.389	2.530	0.106		4.804	3.253	
	13.157	12.683	0.413	2.673		26.396	24.644	0.040	4.512		4.981	4.490	
	12.782	1.138	11.899	0.052		25.004	0.100	22.177	0.088		4.603	0.008	
	13.075	0.285	12.117	0.087		25.802	0.023	22.379	0.013		4.805	0.008	
mean	12.925	7.114	5.604	2.290	mean	25.642	12.611	9.462	4.386	mean	4.795	1.565	
std dev.	0.202	5.999	5.972	3.697	std dev.	0.515	11.686	11.741	7.423	std dev.	0.134	2.151	
C/Co	1.000	0.550	0.434	0.177	C/Co	1.000	0.492	0.369	0.171	C/Co	1.000	0.326	
Act	12.909	6.069	11.127	0.019	Act	25.276	12.496	21.021	0.013	Act	4.763	2.190	
	12.331	12.252	7.332	10.735		24.320	23.773	13.998	18.044		4.563	4.325	
	12.505	8.701	0.019	10.754		24.624	17.642	0.013	19.986		4.631	3.176	
	12.402	11.769	12.012	0.363		24.487	23.942	22.861	0.126		4.610	4.448	
	13.175	12.671	10.625	0.153		25.672	24.716	20.387	0.039		4.752	4.498	
mean	12.664	10.292	8.223	4.405	mean	24.876	20.514	15.656	7.642	mean	4.664	3.727	
std dev.	0.383	2.631	4.916	5.789	std dev.	0.574	5.305	9.361	10.405	std dev.	0.089	1.017	
C/Co	1.000	0.813	0.649	0.348	C/Co	1.000	0.825	0.629	0.307	C/Co	1.000	0.799	
Sterile Control	13.066	1.030	12.388	14.360	Control	26.140	2.211	24.154	26.874	Control	4.961	0.360	
	13.017	12.151	11.774	6.444		25.836	24.407	23.652	12.912		4.870	4.538	
	13.312	11.875	6.454	9.437		26.195	24.208	13.608	18.595		4.948	4.521	
	13.298	10.074	11.970	9.462		26.063	20.869	23.631	18.779		4.879	3.859	
	13.306	10.158	12.250	12.712		26.344	20.778	23.411	23.364		4.952	3.825	
mean	13.200	9.058	10.967	10.483	mean	26.116	18.495	21.691	20.105	mean	4.922	3.421	
std dev.	0.148	4.588	2.534	3.100	std dev.	0.186	9.268	4.527	5.297	std dev.	0.044	1.745	
C/Co	1.000	0.686	0.831	0.794	C/Co	1.000	0.708	0.831	0.770	C/Co	1.000	0.695	

U.S. EPA Microcosm All concen														
135-tmb					124-tmb					123-tmb				
	Day 1	Day 42	Day 73	Day 163		Day 1	Day 42	Day 73	Day 163		Day 1	Day 42		
Act NO3	0.589	0.538	0.107	0.409	Act NO3	1.881	0.090	0.528	1.381	Act NO3	0.587	0.559		
	0.598	0.437	0.262	0.009		1.928	1.441	0.644	0.009		0.602	0.486		
	0.623	0.571	0.123	0.372		1.992	1.826	0.569	1.240		0.623	0.578		
	0.564	0.246	0.555	0.423		1.814	0.923	1.792	1.226		0.568	0.378		
	0.581	0.104	0.540	0.126		1.901	0.433	1.719	0.521		0.595	0.236		
mean	0.593	0.379	0.317	0.268	mean	1.903	0.943	1.050	0.875	mean	0.595	0.447		
std dev.	0.021	0.199	0.219	0.188	std dev.	0.065	0.710	0.646	0.589	std dev.	0.020	0.142		
C/Co	1.000	0.839	0.535	0.452	C/Co	1.000	0.495	0.552	0.460	C/Co	1.000	0.752		
Act	0.596	0.312	0.513	0.008	Act	1.913	1.158	1.693	0.009	Act	0.597	0.427		
	0.571	0.554	0.361	0.373		1.840	1.754	1.285	1.229		0.577	0.550		
	0.580	0.435	0.009	0.437		1.860	1.463	0.009	1.417		0.581	0.500		
	0.562	0.578	0.567	0.344		1.867	1.847	1.853	1.060		0.584	0.585		
	0.591	0.575	0.516	0.080		1.896	1.818	1.701	0.387		0.594	0.567		
mean	0.584	0.481	0.393	0.248	mean	1.875	1.608	1.308	0.820	mean	0.587	0.526		
std dev.	0.010	0.116	0.228	0.191	std dev.	0.029	0.294	0.756	0.597	std dev.	0.009	0.064		
C/Co	1.000	0.840	0.673	0.425	C/Co	1.000	0.858	0.560	0.438	C/Co	1.000	0.896		
Control	0.829	0.074	0.830	0.820	Control	2.007	0.395	2.045	1.966	Control	0.626	0.212		
	0.811	0.581	0.831	0.322		1.958	1.863	2.060	1.174		0.613	0.590		
	0.824	0.588	0.392	0.447		1.986	1.895	1.438	1.493		0.617	0.607		
	0.808	0.518	0.817	0.459		1.955	1.721	2.003	1.519		0.612	0.558		
	0.822	0.510	0.804	0.537		1.993	1.698	1.963	1.694		0.621	0.551		
mean	0.818	0.454	0.575	0.477	mean	1.980	1.514	1.902	1.569	mean	0.618	0.504		
std dev.	0.009	0.215	0.103	0.111	std dev.	0.023	0.632	0.262	0.290	std dev.	0.006	0.165		
C/Co	1.000	0.734	0.929	0.771	C/Co	1.000	0.765	0.961	0.793	C/Co	1.000	0.815		

U.S. EPA Denitrification Study Microcosm Experiment 3 - High concentration BTEX/TMB under high and low oxygen and nitrate conditions using contaminated aquifer material from Nitrate Cell All concentrations mg/L											
benzene	0	1	14	39	82	83	86	111	145	154	173
Elapsed Time (days)	0	1	14	39	82	83	86	111	145	154	173
Low O2 1/10	2.111	1.838	1.919	1.919	1.904	2.016	1.992	2.045	1.967	1.883	1.015
mean	2.101	1.790	1.837	1.998	1.960	1.980	1.818	1.864	2.093	1.883	0.467
std dev	2.092	1.772	1.999	1.918	1.960	1.960	1.905	1.935	2.030	1.883	0.831
C/Co	0.010	0.033	0.081	0.813	0.933	0.907	0.907	0.930	0.966	0.896	0.649
	1.000	0.856	0.813								0.309
											rep1/mean
											rep2/mean
											rep3/mean
STERILE											STERILE
mean	22.482	26.963	23.505	26.806	27.477	27.639	28.982	28.054	29.441	25.742	25.742
std dev	27.136	25.117	26.128	28.971	25.485	27.847	27.875	25.092	26.823	26.450	26.450
C/Co	24.784	27.224	24.630	27.889	28.481	27.743	28.929	25.573	28.132	27.096	27.096
	24.801	26.435	24.754	1.125	1.068	1.119	1.166	1.031	1.175	1.093	1.093
	2.327	1.149	1.316								rep1/mean
	1.000	1.066	0.996								rep2/mean
											rep3/mean
Low O2	20.979	22.662	22.348	31.400	23.281	25.419	25.213	23.240	20.579	18.266	18.266
mean	24.137	22.773	23.943	24.286	22.985	23.623	24.960	22.705	20.255	20.255	20.255
std dev	21.288	22.850	26.272	27.848	23.133	24.521	25.087	23.240	21.642	19.262	19.262
C/Co	1.741	0.084	3.065	1.258	1.045	1.108	1.133	1.050	0.978	0.870	0.870
	1.000	1.029	1.123								rep1/mean
											rep2/mean
											rep3/mean
High O2	19.643	16.490	16.948	15.642	12.911	15.642	14.346	13.364	14.954	14.629	5.602
mean	17.164	12.024	15.388	18.101	13.535	14.031	14.462	14.629	4.050	4.050	4.050
std dev	17.894	14.200	14.456	16.872	13.941	13.688	14.708	14.629	4.826	4.826	4.826
C/Co	1.8234	14.238	15.587	0.925	0.765	0.751	0.807	0.802	0.265	0.265	0.265
	1.274	2.233	1.259	0.708							rep1/mean
	1.000	0.781	0.855								rep2/mean
											rep3/mean
Unamended	22.303	24.877	25.350	27.799	23.756	24.764	24.764	24.764	24.764	24.764	24.764
mean	22.640	24.582	26.528	26.145	26.145	26.145	26.145	26.145	26.145	26.145	26.145
std dev	23.357	24.403	26.028	26.972	26.972	26.972	26.972	26.972	26.972	26.972	26.972
C/Co	0.538	0.239	0.591	1.185	1.066	1.066	1.066	1.066	1.066	1.066	1.066
	1.000	1.082	1.141								1.087
											C/Co

U.S. EPA Denitrif Microcosm Exper All concentration												ethylbenzene Elapsed Time (da)				
1	14	39	82	83	96	111	145	154	160	173	1	14	39	82	83	
2.983	2.560	2.290		0.578	0.552	0.627	0.493	0.400	0.476	0.000	Low O2 1/10	1.331	1.058	1.105	0.831	
2.984	2.538	2.473		2.873	2.351	2.564	2.834		0.355	0.040		1.549	1.018	0.970	1.226	
2.935	2.514	0.770										1.394	0.900	0.609		
2.954	2.537	1.844		1.726	1.452	1.596	1.664	0.400	0.416	0.020	mean	1.425	0.991	0.961	1.029	
0.016	0.023	0.935									std dev.	0.112	0.082	0.148		
1.000	0.859	0.624		0.584	0.491	0.540	0.563	0.135	0.141	0.007	C/Co	1.000	0.696	0.675	0.722	
1.003	0.867	0.775		0.196	0.187	0.212	0.167	0.135	0.161	0.000						
1.003	0.859	0.837		0.973	0.796	0.868	0.959		0.120	0.014						
0.994	0.851	0.261														
33.999	41.337	35.219		40.654	42.629	40.913	44.723	39.065	40.257	39.396	STERILE	4.173	4.929	4.276	4.928	
42.478	38.072	39.776		43.226	44.287	40.671	42.266	36.537	39.526	40.073		5.551	4.118	4.827	4.260	
38.161	40.891	36.994										4.984	4.242	4.496		
38.212	40.100	37.330		41.940	43.458	40.792	43.495	37.801	39.892	39.735	mean	4.903	4.430	4.566	4.594	
4.239	1.770	2.297									std dev.	0.693	0.437	0.331		
1.000	1.049	0.977		1.098	1.137	1.068	1.138	0.989	1.044	1.040	C/Co	1.000	0.904	0.931	0.937	
0.890	1.082	0.922		1.064	1.116	1.071	1.170	1.022	1.054	1.031						
1.112	0.996	1.041		1.131	1.159	1.064	1.106	0.956	1.034	1.049						
0.999	1.070	0.966														
28.148	30.090	30.255		43.440	31.257	32.697	34.722	30.989	19.465	14.627	Low O2	3.753	4.131	3.996	5.411	
32.811	30.852	31.599		32.919	30.526	31.524	33.818		18.782	19.597		4.249	4.223	4.079	4.239	
28.650	31.496	39.126										3.851	4.110	5.079		
29.870	30.813	33.660		38.180	30.892	32.111	34.270	30.989	19.124	17.112	mean	3.951	4.155	4.385	4.625	
2.560	0.704	4.781									std dev.	0.263	0.060	0.603		
1.000	1.032	1.127		1.278	1.034	1.075	1.147	1.037	0.640	0.573	C/Co	1.000	1.052	1.110	1.221	
0.942	1.007	1.013		1.454	1.048	1.095	1.162	1.037	0.652	0.490						
1.096	1.033	1.058		1.102	1.022	1.055	1.132		0.629	0.656						
0.959	1.054	1.310														
25.112	18.971	16.290	11.336	14.443	12.102	11.032	13.546	13.860	2.223		High O2	2.493	1.380	1.608	0.778	0.902
21.353	10.594	14.637		17.709	12.062	12.214	12.031		0.771			2.308	1.257	1.367	1.262	
22.973	12.197	13.492										2.524	1.099	1.114		
23.148	13.254	14.673	11.336	16.078	12.082	11.623	12.789	13.860	1.497		mean	2.442	1.245	1.363	0.778	1.082
1.865	3.317	1.399									std dev.	0.117	0.141	0.247		
1.000	0.573	0.643	0.490	0.695	0.522	0.502	0.553	0.599	0.065		C/Co	1.000	0.510	0.558	0.319	0.443
1.085	0.733	0.704	0.490	0.624	0.523	0.477	0.585	0.599	0.096							
0.923	0.458	0.641		0.785	0.521	0.528	0.520		0.033							
0.993	0.527	0.583														
31.547	34.138	34.640		37.585	32.579					35.740	Unamended	3.974	4.410	4.566	4.815	
32.303	33.847	34.833		35.464	34.090					34.549		4.037	4.500	4.549	4.712	
33.516	34.216	35.161										4.147	4.465	4.634		
32.455	34.068	34.878		36.515	33.335					35.145	mean	4.053	4.458	4.583	4.764	
0.993	0.194	0.263									std dev.	0.088	0.045	0.045		
1.000	1.050	1.075		1.125	1.027					1.083	C/Co	1.000	1.100	1.131	1.175	

U.S. EPA Denitrif Microcosm Expe All concentration	145	154	160	173	123-3mb Elapsed Time (day)	1	14	39	82	83	96	111	145	154	160	173
	4.028	4.080	3.824	1.926	Low O2 1/10	0.901	1.043	1.168		1.004	1.082	1.088	1.110	1.078	1.068	1.114
	4.718		3.175	1.388		1.017	1.055	1.031		1.142	1.161	1.095	1.302		1.028	1.109
	4.374	4.050	3.500	1.658	mean std dev	0.960	1.043	1.062		1.073	1.122	1.092	1.206	1.078	1.048	1.112
	1.250	1.168	1.000	0.474	C/Co	0.058	0.012	0.094		1.117	1.168	1.137	1.256	1.123	1.091	1.157
						1.000	1.086	1.106								
	1.743	1.487	1.474	1.511	STERILE	0.439	0.468	0.408		0.433	0.467	0.428	0.489	0.438	0.428	0.444
	1.954	1.333	1.376	1.378		0.477	0.438	0.530		0.456	0.514	0.438	0.578	0.438	0.403	0.408
	1.849	1.415	1.425	1.445	mean std dev	0.428	0.450	0.463		0.445	0.481	0.434	0.539	0.438	0.416	0.426
	1.188	0.910	0.916	0.929	C/Co	0.028	0.015	0.061		0.992	1.085	0.968	1.202	0.978	0.929	0.951
						1.000	1.008	1.042								
	3.828	4.245	4.138	4.481	Low O2	1.023	1.215	1.152		1.421	1.306	1.274	1.067	1.198	1.155	1.285
	4.060		3.985	4.102		1.105	1.241	1.150		1.152	1.254	1.102	1.136		1.113	1.152
	3.945	4.245	4.067	4.282	mean std dev	1.037	1.162	1.378		1.287	1.280	1.188	1.102	1.196	1.134	1.209
	1.059	1.140	1.092	1.152	C/Co	0.044	0.040	0.131		1.219	1.213	1.128	1.044	1.136	1.075	1.145
						1.000	1.143	1.183								
	5.223	6.608	3.714		High O2	0.820	1.151	1.454	1.153	1.231	1.445	1.132	1.482	1.884	1.031	
	4.960		3.949			0.903	1.204	1.234		1.402	1.264	1.167	1.389		1.118	
	5.092	6.608	3.832		mean std dev	0.885	1.297	1.129		1.317	1.355	1.150	1.438	1.864	1.075	
	1.851	2.143	1.243		C/Co	0.044	0.074	0.186		1.514	1.558	1.322	1.651	2.187	1.236	
						1.000	1.400	1.484	1.326							
					Unamended	0.798	1.035	1.086		1.160	1.085					1.215
						0.760	1.058	1.088		1.125	1.214					1.189
					mean std dev	0.759	1.016	1.093		1.143	1.150					1.202
					C/Co	0.772	1.038	1.079		1.478	1.488					1.556
						0.022	0.021	0.010								
						1.000	1.342	1.397								

U.S. EPA Dantiriff Microcosm Expt All concentrations	naphthalene		14		39		82		83		96		111		145		154		160		173		total BTEKTMB Elapsed Time (days)	
	1	14	39	82	83	96	111	145	154	160	173	1	14	39										
Elapsed Time (day)	1.489	1.683	1.753	1.417	1.417	1.649	1.655	1.565	1.654	1.511	1.574	18.982	20.300	21.048										
Low O2 1/10	1.622	1.724	1.575	1.619	1.619	1.765	1.643	2.010	1.654	0.277	1.335	20.510	20.086	19.005										
mean	1.513	1.650	1.541	1.518	1.518	1.707	1.649	1.788	1.654	0.804	1.455	19.214	19.417	17.228										
std dev.	0.071	0.086	0.123	0.037	0.114	0.107	0.107	0.160	1.073	0.580	0.844	19.562	19.938	19.093										
C/Co	1.000	1.094	1.053	0.985	0.985	1.107	1.070	1.160	1.073	0.580	0.844	1.000	1.019	0.976										
STERILE	0.979	0.777	0.854	0.842	0.842	0.748	0.709	0.815	0.766	0.772	0.747	76.732	93.443	78.988										
mean	0.807	0.728	1.112	0.714	0.714	1.076	0.710	1.211	0.750	0.707	0.728	95.452	86.285	89.830										
std dev.	0.785	0.741	1.009	0.778	0.778	0.912	0.710	1.013	0.758	0.740	0.738	86.200	92.288	83.284										
C/Co	0.857	0.749	0.992	0.908	0.908	1.064	0.828	1.182	0.884	0.863	0.861	86.128	90.675	84.031										
mean	1.000	0.874	1.157	0.908	0.908	1.064	0.828	1.182	0.884	0.863	0.861	9.360	3.837	5.457										
std dev.	1.000	0.874	1.157	0.908	0.908	1.064	0.828	1.182	0.884	0.863	0.861	1.000	1.053	0.978										
C/Co	1.000	0.874	1.157	0.908	0.908	1.064	0.828	1.182	0.884	0.863	0.861	0.891	1.085	0.917										
Low O2	1.776	2.250	1.943	2.238	2.238	2.166	2.133	1.765	2.017	1.834	2.035	73.722	61.349	79.658										
mean	1.909	2.075	1.929	1.788	1.788	2.043	1.811	1.853	2.017	1.728	1.872	84.036	82.764	83.201										
std dev.	1.762	1.914	2.279	2.013	2.013	2.105	1.972	1.809	2.017	1.760	1.954	74.888	62.363	101.133										
C/Co	0.081	0.080	0.168	1.109	1.109	1.159	1.086	0.998	1.111	0.980	1.076	77.552	62.159	87.997										
High O2	1.433	1.902	2.353	1.508	1.679	2.338	1.470	1.910	2.681	1.592	1.952	5.646	0.729	11.513										
mean	1.583	1.915	2.061	1.948	1.948	2.038	1.611	2.179	2.681	1.438	1.952	1.000	1.059	1.135										
std dev.	1.507	2.124	1.855	1.508	1.508	1.814	1.541	2.045	2.681	1.515	1.954	65.067	58.008	62.936										
C/Co	0.080	0.125	0.250	0.988	0.988	1.449	1.020	1.353	1.774	1.003	1.003	58.348	48.107	55.431										
Unamended	1.342	1.850	1.772	1.872	1.872	1.810	1.810	1.810	1.810	1.810	1.810	61.601	53.438	51.544										
mean	1.348	1.860	1.767	1.757	1.757	2.032	1.611	2.179	2.681	1.438	1.952	3.361	4.955	5.791										
std dev.	1.352	1.838	1.783	1.815	1.815	1.921	1.815	1.921	2.681	1.515	1.954	1.000	0.962	0.916										
C/Co	0.013	0.030	0.024	1.342	1.342	1.421	1.421	1.421	1.421	1.003	1.076	76.804	85.672	87.689										
Unamended	1.342	1.850	1.772	1.872	1.872	1.810	1.810	1.810	1.810	1.810	1.810	79.484	85.665	88.739										
mean	1.348	1.860	1.767	1.757	1.757	2.032	1.611	2.179	2.681	1.438	1.952	80.366	85.557	89.064										
std dev.	1.352	1.838	1.783	1.815	1.815	1.921	1.815	1.921	2.681	1.515	1.954	78.915	85.688	88.491										
C/Co	0.013	0.030	0.024	1.342	1.342	1.421	1.421	1.421	1.421	1.003	1.076	1.000	0.160	0.730										
Unamended	1.342	1.850	1.772	1.872	1.872	1.810	1.810	1.810	1.810	1.810	1.810	1.000	1.086	1.121										

U.S. EPA Denitrif Microcosm Expt All concentration	111	145	154	160	173	nitrite (mg/L) Elapsed Time (days)	1	14	39	62	83	96	111	145	154.0	160	173
	63.92	64.87	50.3	70.08	49.32	Low O2 1/10	0.2	0.2	0.54		0.2	0.2	0.2	0.2	0.2	0.2	0.2
	74.51	68.41		63.6	47.36		0.2	0.2	0.21		0.2	0.2	0.2	0.2		0.2	0.2
	69.215	67.140	50.300	66.840	48.340	mean	0.200	0.200	0.317		0.200	0.200	0.200	0.200	0.200	0.200	0.200
	0.702	0.681	0.510	0.678	0.480	std dev	0.000	0.000	0.193		1.000	1.000	1.000	1.000	1.000	1.000	1.000
						C/Co	1.000	1.000	1.583								
	117.220	113.540	96.870	105.630	107.020	STERILE	0.2	0.2	0.2		0.2	0.2	0.2	0.2	0.2	0.2	0.2
	121.700	108.950	114.200	112.740	123.390		0.2	0.2	0.2		0.2	0.2	0.2	0.2	0.2	0.2	0.2
	119.460	111.245	108.535	108.185	115.205	mean	0.2	0.2	0.2		0.2	0.2	0.2	0.2	0.2	0.2	0.2
	1.012	0.942	0.903	0.925	0.978	std dev	0.000	0.000	0.000		1.000	1.000	1.000	1.000	1.000	1.000	1.000
						C/Co	1.000	1.000	1.000								
	27.660	33.100	20.270	0.260	0.260	Low O2	0.2	0.2	0.2		0.2	0.2	0.960	9.940	0.7	0.600	0.200
	27.160	22.940		20.780	0.260		0.2	0.2	0.2		0.2	0.2	1.460	8.550	1.000	1.000	0.200
	27.410	28.020	20.270	10.525	0.260	mean	0.200	0.200	0.200		0.200	0.200	1.210	9.245	0.670	0.900	0.200
	0.281	0.287	0.208	0.108	0.003	std dev	0.000	0.000	0.000		1.000	1.000	6.050	48.225	3.350	4.500	1.000
						C/Co	1.000	1.000	1.000								
	44.510	36.200	37.870	33.260		High O2	0.2	0.2	0.2		0.2	0.2	0.2	0.2	0.2	0.200	0.2
	54.550	48.000		44.470			0.2	0.2	0.2		0.2	0.2	0.2	0.2	0.2	0.200	0.200
	49.530	42.100	37.870	38.875		mean	0.200	0.200	0.200		0.200	0.200	0.200	0.200	0.200	0.200	0.200
	0.596	0.507	0.458	0.468		std dev	0.000	0.000	0.000		1.000	1.000	1.000	1.000	1.000	1.000	1.000
						C/Co	1.000	1.000	1.000								
						Unamended											
						mean											
						std dev											
						C/Co											

U.S. EPA Denitrif Microcosm Exper All concentrations	dissolved oxygen (mg/L)										
	1	14	38	82	83	86	111	145	154	160	173
Elapsed Time (days)											
Low O2 1/10	0.530 0.810 0.450	0.330 0.160 0.450	0.330 0.330 0.480		0.520 0.650	0.530 0.410 0.410	0.570 0.450 0.410	0.410 0.410	11.160 1.100	10.160 1.100	0.920 0.600
mean	4.900	0.597	0.313		0.585	0.470	0.510	0.410	11.160	5.640	0.760
std dev.	0.169	0.146	0.092		0.980	0.788	0.855	0.687	18.704	9.453	1.274
C/Co	1.000	0.525	0.642								
STERILE											
mean	4.400	1.520	2.140		0.560	0.980	0.450	0.570	16.210	22.400	20.480
std dev.	4.970	0.780	1.850		0.610	0.240	0.570	0.160	16.700	21.670	19.760
C/Co	5.210	0.250	1.970		0.585	0.610	0.510	0.365	16.455	22.035	20.120
mean	4.900	0.650	1.987		0.120	0.126	0.105	0.075	3.386	4.534	4.140
std dev.	4.418	0.638	1.146		0.115	0.202	0.093	0.117	3.335	4.609	4.214
C/Co	1.000	0.175	0.409		0.126	0.048	0.117	0.033	3.436	4.458	4.066
mean	0.905	0.313	0.440								
std dev.	1.023	0.180	0.381								
C/Co	1.072	0.051	0.405								
Low O2	0.450 0.770 0.610	0.490 0.620 0.660	0.490 0.450 0.580		0.560 0.610	0.200 0.370 0.285	0.200 0.570 0.385	0.370 0.410 0.390	11.080 0.490	0.890 0.640	0.480 0.640
mean	4.900	0.610	0.507		0.585	0.467	0.631	0.639	18.164	0.967	0.918
std dev.	0.160	0.069	0.067		0.959						
C/Co	1.000	0.967	0.831								
High O2	1.870 8.110 4.150	1.030 1.150 1.150	1.690 1.480 1.520		0.740 0.480	0.690 0.240	0.430 0.450	0.610 0.610	16.290 8.100	8.100 9.650	
mean	26.500	4.043	1.110		0.610	0.465	0.440	0.610	16.290	8.875	
std dev.	2.122	0.068	0.112		0.115	0.115	0.109	0.151	4.028	2.185	
C/Co	1.000	0.275	0.387								
Unamended											
mean	0.120	0.450	0.660		0.390	0.330					0.600
std dev.	0.370	0.410	0.450		0.520	0.330					0.520
C/Co	0.330	0.740	0.530		0.455	0.330					0.560
mean	0.273	0.533	0.547		1.665	1.207	0.000	0.000	0.000	0.000	2.048
std dev.	0.134	0.180	0.106								
C/Co	1.000	1.851	2.000								

BTEX/TMB Concentrations in Gasoline-Saturated Water (water used to set up microcosms = day 0)									
	gas-sat A	gas-sat B	gas-sat D	10x dil.	gas-sat	mean	s.d.		
Ben	28.840	28.846	26.986		3.309	28.161	1.013		
Tol	44.278	44.835	41.748		5.120	43.620	1.645		
Eben	5.913	6.114	5.602		0.692	5.876	0.258		
m+p-Xyl	12.408	12.845	11.761		1.452	12.337	0.545		
o-Xyl	5.511	5.857	5.229		0.641	5.468	0.218		
135-TMB	0.521	0.554	0.508		0.065	0.527	0.025		
124-TMB	1.874	1.982	1.777		0.223	1.878	0.103		
123-TMB	0.524	0.551	0.508		0.062	0.528	0.022		
Naph	0.904	0.889	0.872		0.148	0.888	0.016		
BTEX/TMB Concentrations in water in contact with "washed" aquifer material									
Ben	1.000	2.000	3.000		4.000	5.000			
Tol	0.089	0.090	0.084		0.087	0.088			
Eben	1.537	1.302	0.597		0.188	0.118			
m+p-Xyl	4.416	3.807	2.123		1.151	0.672			
o-Xyl	1.630	1.560	0.841		3.573	2.161			
135-TMB	1.169	1.093	0.636		1.461	0.856			
124-TMB	3.943	3.637	2.714		1.066	0.842			
123-TMB	1.104	1.002	0.697		3.578	2.721			
Naph	1.647	1.521	1.230		0.987	0.697			

U.S. EPA Denitrification Study Dehydrogenase Activity Assay Aerobic Conditions		bl	bl	ster unam	ster unam	unam	unam	pos	pos	g.s.	g.s.	1/10 g.s.	1/10 g.s.
BK - Day 0 on 9-9-97													
4D - Day 0 on 9-10-97													
3D - Day 0 on 9-10-97													
Treatment													
BK, DAY 0													
Pan #	1.000	2.000	3.000	4.000	5.000	6.000	7.000	8.000	9.000	10.000	11.000	12.000	
Dry Wt. (g)	0.384	0.397	0.232	0.319	0.157	0.260	0.313	0.256	0.366	0.299	0.328	0.464	
Spec 480 nm	0.000	-0.001	0.002	0.002	0.005	0.003	0.003	0.004	0.001	0.003	0.002	0.002	
ug INT formazan/g	0.000	-0.312	1.068	0.778	3.955	1.432	1.189	1.939	0.169	1.245	0.754	0.534	
ug INT formazan/g (bl corr.)		1.224	4.111	0.934		1.588	1.345	2.095	0.325	1.401	0.910	0.690	
4S, DAY 0													
Pan #	1.000	2.000	3.000	4.000	5.000	6.000	7.000	8.000	9.000	10.000	11.000	12.000	
Dry Wt. (g)	0.367	0.482	0.502	0.494	0.616	0.453	0.363	0.552	0.532	0.442	0.342	0.532	
Spec 480 nm	0.037	0.038	0.046	0.051	0.049	0.044	0.047	0.048	0.050	0.051	0.047	0.027	
ug INT formazan/g	12.492	9.776	11.362	12.781	9.849	12.032	16.061	10.772	11.647	14.287	17.009	6.286	
ug INT formazan/g (bl corr.)			0.228	1.647	-1.285	0.898	4.927	-0.362	0.513	3.153	5.875	-4.848	
4D, DAY 0													
Pan #	1.000	2.000	3.000	4.000	5.000	6.000	7.000	8.000	9.000	10.000	11.000	12.000	
Dry Wt. (g)	0.173	0.291	0.283	0.433	0.343	0.240	0.391	0.366	0.441	0.278	0.536	0.353	
Spec 480 nm	0.000	0.000	0.002	0.003	0.014	0.009	0.009	0.017	0.026	0.024	0.027	0.015	
ug INT formazan/g	0.000	0.000	0.877	0.857	5.062	4.649	2.851	5.453	7.303	10.698	6.245	5.271	
ug INT formazan/g (bl corr.)			0.877	0.857	5.062	4.649	2.851	5.453	7.303	10.698	6.245	5.271	
3D, DAY 0													
Pan #	17.000	18.000	19.000	20.000	21.000	22.000	23.000	24.000	25.000	26.000	27.000	28.000	
Dry Wt. (g)	0.350	0.531	0.208	0.501	0.593	0.337	0.514	0.176	0.452	0.260	0.621	0.481	
Spec 480 nm	0.048	0.052	0.007	0.012	0.072	0.061	0.062	0.040	0.074	0.039	0.092	0.065	
ug INT formazan/g	17.013	12.128	4.179	2.965	15.030	22.429	14.951	28.169	20.294	18.581	18.346	16.392	
ug INT formazan/g (bl corr.)			-10.392	-11.606	0.460	7.858	0.380	13.589	5.723	4.010	3.775	1.821	
BK, DAY 7													
Pan #	1.000	2.000	3.000	4.000	5.000	6.000	7.000	8.000	9.000	10.000	11.000	12.000	
Dry Wt. (g)	0.324	0.396	0.327	0.302	0.364	0.249	0.457	0.427	0.301	0.347	0.321	0.380	
Spec 480 nm	0.017	0.016	0.018	0.008	0.020	0.036	0.063	0.030	0.075	0.118	0.019	0.046	
ug INT formazan/g	6.494	5.000	6.825	3.284	6.798	17.931	17.084	8.703	30.907	42.076	7.325	15.015	
ug INT formazan/g (bl corr.)			1.076	-2.463	1.052	12.184	11.337	2.956	25.160	36.329	1.579	9.268	

U.S. EPA Denitrification S									
Dehydrogenase Activity A									
Aerobic Conditions									
Treatment	g.s.*glu	g.s.*glu	1/10 g.s.*glu	1/10 g.s.*glu	ster amen	ster amen	1/10 g.s.*glu	ster amen	INT FORMAZAN STANDARD CURVE
BK - Day 0 on 9-9-97									
4D - Day 0 on 9-10-97									
3D - Day 0 on 9-10-97									
BK, DAY 0									
Pan #	13.000	14.000	15.000	16.000	23.000	24.000			
Dry Wt. (g)	0.276	0.408	0.205	0.403	0.717	0.717			
Spec 480 nm	0.003	0.005	0.002	0.000	0.051	0.049			
ug INT formazan/ug	1.345	1.517	1.210	0.000					
ug INT formazan/g (bl corr.)	1.501	1.673	1.366	0.156					
4S, DAY 0									
Pan #	13.000	14.000	15.000	16.000	17.000	18.000			
Dry Wt. (g)	0.465	0.517	0.519	0.574	0.645	0.745			
Spec 480 nm	0.050	0.052	0.049	0.052	0.045	0.047			
ug INT formazan/ug	13.328	12.454	11.695	11.216					
ug INT formazan/g (bl corr.)	2.194	1.320	0.561	0.082					
4D, DAY 0									
Pan #	13.000	14.000	15.000	16.000	19.000	20.000			
Dry Wt. (g)	0.416	0.364	0.325	0.166	0.739	0.740			
Spec 480 nm	0.024	0.024	0.027	0.012	0.053	0.053			
ug INT formazan/ug	7.145	8.170	10.307	8.949					
ug INT formazan/g (bl corr.)	7.145	8.170	10.307	8.949					
3D, DAY 0									
Pan #	29.000	30.000	31.000	32.000	21.000	22.000			
Dry Wt. (g)	0.233	0.326	0.169	0.443	0.483	0.623			
Spec 480 nm	0.038	0.047	0.035	0.074	0.047	0.051			
ug INT formazan/ug	20.203	17.837	25.700	20.706	0.097	0.082			
ug INT formazan/g (bl corr.)	5.632	3.267	11.129	6.136					
BK, DAY 7									
Pan #	13.000	14.000	15.000	16.000					
Dry Wt. (g)	0.313	0.399	0.325	0.302					
Spec 480 nm	0.137	0.056	0.080	0.094					
ug INT formazan/ug	54.168	17.399	30.473	38.518					
ug INT formazan/g (bl corr.)	48.421	11.652	24.726	32.772					

Treatment	bl	bl	ster unam	ster unam	unam	unam	unam	pos	pos	g.s.	g.s.	1/10 g.s.	1/10 g.s.
4S, DAY 6													
Pan #	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000	10,000	11,000	12,000	
Dry Wt. (g)	0.495	0.457	0.489	0.549	0.421	0.526	0.514	0.575	0.575	0.656	0.626	0.737	
Spec 480 nm	0.040	0.043	0.047	0.046	0.105	0.122	0.126	0.112	0.157	0.153	0.151	0.141	
ug INT formazan/g	10,010	11,666	11,916	10,374	30,902	28,758	30,372	33,829	28,882	29,880	29,880	23,693	
ug INT formazan/g (bl corr.)		1,078	-0,464		20,064	17,921	18,534	22,991	18,045	19,042	12,855		
4D, DAY 6													
Pan #	17,000	18,000	19,000	20,000	21,000	22,000	23,000	24,000	25,000	26,000	27,000	28,000	
Dry Wt. (g)	0.338	0.414	0.306	0.304	0.314	0.297	0.335	0.423	0.317	0.413	0.393	0.337	
Spec 480 nm	0.013	0.015	0.020	0.015	0.078	0.084	0.135	0.122	0.217	0.302	0.164	0.131	
ug INT formazan/g	4,766	4,485	8,088	6,110	30,771	35,035	49,860	35,693	84,717	90,603	51,759	48,110	
ug INT formazan/g (bl corr.)		3,463	1,485		26,146	30,410	45,234	31,068	80,091	85,977	47,133	43,484	
3D, DAY 6													
Pan #	33,000	34,000	35,000	36,000	37,000	38,000	39,000	40,000	41,000	42,000	43,000	44,000	
Dry Wt. (g)	0.369	0.256	0.308	0.489	0.438	0.451	0.239	0.620	0.583	0.325	0.324	0.439	
Spec 480 nm	0.025	0.018	0.034	0.061	0.079	0.104	0.133	0.186	0.192	0.184	0.069	0.107	
ug INT formazan/g	8,399	8,723	13,674	15,443	22,343	28,584	68,847	37,174	40,795	70,132	26,356	30,192	
ug INT formazan/g (bl corr.)		5,113	6,882		13,781	20,023	60,266	28,613	32,234	61,570	17,795	21,631	
BK, DAY 14													
Pan #	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000	10,000	11,000	12,000	
Dry Wt. (g)	0.286	0.343	0.505	0.449	0.365	0.541	0.460	0.457	0.339	0.524	0.335	0.510	
Spec 480 nm	0.014	0.012	0.021	0.025	0.058	0.039	0.035	0.102	0.094	0.128	0.053	0.032	
ug INT formazan/g	6,057	4,335	5,150	6,903	19,684	8,933	9,429	27,666	34,379	30,288	20,707	7,777	
ug INT formazan/g (bl corr.)		-0,046	1,707		14,488	3,737	4,233	22,470	29,183	25,092	15,511	2,581	
4S, DAY 13													
Pan #	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000	10,000	11,000	12,000	
Dry Wt. (g)	0.663	0.525	0.571	0.505	0.618	0.659	0.615	0.518	0.635	0.526	0.682	0.843	
Spec 480 nm	0.045	0.045	0.052	0.048	0.126	0.120	0.126	0.094	0.142	0.123	0.146	0.141	
ug INT formazan/g	8,403	10,616	11,277	11,767	25,244	22,560	25,400	22,470	27,701	28,950	26,538	20,729	
ug INT formazan/g (bl corr.)		1,768	2,258		15,734	13,051	15,890	12,961	18,192	19,441	17,029	11,220	
4D, DAY 13													
Pan #	17,000	18,000	19,000	20,000	21,000	22,000	23,000	24,000	25,000	26,000	27,000	28,000	
Dry Wt. (g)	0.446	0.541	0.453	0.444	0.467	0.457	0.531	0.482	0.776	0.490	0.486	0.444	
Spec 480 nm	0.021	0.012	0.000	0.031	0.059	0.097	0.174	0.232	0.446	0.287	0.132	0.108	
ug INT formazan/g	5,835	2,746	0,000	8,659	15,650	26,316	40,561	59,587	71,159	72,495	33,665	30,152	
ug INT formazan/g (bl corr.)		-4,290	4,368		11,360	22,025	36,270	55,296	66,866	68,205	29,375	25,961	
3D, DAY 13													
Pan #	33,000	34,000	35,000	36,000	37,000	38,000	39,000	40,000	41,000	42,000	43,000	44,000	
Dry Wt. (g)	0.432	0.388	0.306	0.340	0.317	0.427	0.353	0.393	0.408	0.507	0.390	0.342	
Spec 480 nm	0.055	0.056	0.038	0.036	0.074	0.128	0.128	0.109	0.187	0.205	0.095	0.123	
ug INT formazan/g	15,756	17,897	15,398	13,131	28,963	37,124	44,892	34,383	56,748	50,067	30,174	44,525	
ug INT formazan/g (bl corr.)		-1,429	-3,695		12,136	20,298	28,065	17,556	39,921	33,240	13,348	27,698	

Treatment	g.s.+glu	g.s.+glu	1/10 g.s.+glu	1/10 g.s.+glu	ster amen	ster amen														
4S, DAY 6																				
Pan #	13.000	14.000	15.000	16.000																
Dry Wt. (g)	0.591	0.640	0.589	0.671																
Spec 480 nm	0.104	0.154	0.125	0.119																
ug INT formazan/g	21.795	29.826	26.302	21.985																
ug INT formazan/g (bl corr.)	10.957	18.988	15.465	11.147																
4D, DAY 6																				
Pan #	29.000	30.000	31.000	32.000																
Dry Wt. (g)	0.354	0.522	0.398	0.349																
Spec 480 nm	0.303	0.347	0.184	0.162																
ug INT formazan/g	105.908	82.408	57.268	57.467																
ug INT formazan/g (bl corr.)	101.282	77.783	52.643	52.842																
3D, DAY 6																				
Pan #	45.000	46.000	47.000	48.000																
Dry Wt. (g)	0.483	0.511	0.426	0.415																
Spec 480 nm	0.291	0.204	0.218	0.177																
ug INT formazan/g	74.694	49.472	63.376	52.846																
ug INT formazan/g (bl corr.)	66.132	40.910	54.814	44.284																
BK, DAY 14																				
Pan #	13.000	14.000	15.000	16.000																
Dry Wt. (g)	0.396	0.375	0.527	0.541																
Spec 480 nm	0.102	0.154	0.091	0.062																
ug INT formazan/g	31.907	50.939	21.374	14.204																
ug INT formazan/g (bl corr.)	26.711	45.742	16.178	9.008																
4S, DAY 13																				
Pan #	13.000	14.000	15.000	16.000																
Dry Wt. (g)	0.781	0.633	0.766	0.727																
Spec 480 nm	0.171	0.154	0.138	0.125																
ug INT formazan/g	27.108	30.161	22.305	21.313																
ug INT formazan/g (bl corr.)	17.599	20.651	12.796	11.804																
4D, DAY 13																				
Pan #	29.000	30.000	31.000	32.000																
Dry Wt. (g)	0.482	0.498	0.568	0.646																
Spec 480 nm	0.301	0.220	0.204	0.222																
ug INT formazan/g	77.325	54.756	44.482	42.576																
ug INT formazan/g (bl corr.)	73.034	50.466	40.192	38.286																
3D, DAY 13																				
Pan #	45.000	46.000	47.000	48.000																
Dry Wt. (g)	0.336	0.255	0.405	0.492																
Spec 480 nm	0.265	0.113	0.250	0.169																
ug INT formazan/g	97.611	54.850	76.390	42.567																
ug INT formazan/g (bl corr.)	80.784	38.023	59.563	25.741																

Treatment	bl	bl	ster unam	ster unam	unam	unam	pos	pos	g.s.	g.s.	1/10 g.s.	1/10 g.s.
BK, DAY 28												
Pan #	1.000	2.000	3.000	4.000	5.000	6.000	7.000	8.000	9.000	10.000	13.000	11.000
Dry Wt. (g)	0.469	0.381	0.497	0.489	0.536	0.755	0.579	0.691	0.714	0.586	0.443	0.614
Spec 480 nm	0.016	0.002	0.016	0.018	0.016	0.069	0.042	0.093	0.175	0.159	0.128	0.038
ug INT formazan/g	4.224	0.650	3.989	4.556	3.700	11.327	8.993	16.667	30.357	33.634	35.808	7.670
ug INT formazan/g (bl corr.)			1.552	2.119	1.264	8.890	6.557	14.230	27.920	31.197	33.371	5.233
4S, DAY 27												
Pan #	1.000	2.000	3.000	4.000	5.000	6.000	7.000	8.000	9.000	10.000	11.000	12.000
Dry Wt. (g)	0.513	0.570	0.481	0.761	0.827	0.582	0.670	0.558	0.634	0.661	0.635	0.770
Spec 480 nm	0.041	0.043	0.045	0.045	0.146	0.105	0.115	0.106	0.135	0.123	0.120	0.138
ug INT formazan/g	9.908	9.343	11.589	7.325	21.877	22.356	21.271	23.527	26.398	23.054	23.413	22.201
ug INT formazan/g (bl corr.)			1.963	-2.301	12.251	12.730	11.646	13.902	16.772	13.429	13.787	12.575
4D, DAY 27												
Pan #	17.000	18.000	19.000	20.000	21.000	22.000	23.000	24.000	25.000	26.000	27.000	28.000
Dry Wt. (g)	0.510	0.567	0.799	0.587	0.629	0.611	0.509	0.739	0.661	0.610	0.746	0.567
Spec 480 nm	0.020	0.024	0.072	0.024	0.082	0.102	0.198	0.511	0.347	0.346	0.177	0.160
ug INT formazan/g	4.856	5.246	11.163	5.066	16.141	20.683	48.149	85.560	65.019	70.297	29.399	34.943
ug INT formazan/g (bl corr.)			6.112	0.015	11.090	15.632	43.098	80.509	59.968	65.246	24.348	29.892
3D, DAY 27												
Pan #	33.000	34.000	35.000	36.000	37.000	38.000	39.000	40.000	41.000	42.000	43.000	44.000
Dry Wt. (g)	0.458	0.463	0.592	0.421	0.562	0.443	0.518	0.531	0.511	0.681	0.560	0.588
Spec 480 nm	0.046	0.040	0.068	0.079	0.144	0.124	0.141	0.166	0.194	0.192	0.154	0.128
ug INT formazan/g	12.431	10.693	14.224	23.267	31.762	34.650	33.705	38.747	47.074	34.935	34.047	26.957
ug INT formazan/g (bl corr.)			2.662	11.705	20.201	23.088	22.144	27.185	35.513	23.373	22.485	15.395

Treatment	g.s.+glu	g.s.+glu	1/10 g.s.+glu	1/10 g.s.+glu	ster	ster	ster	ster	ster	ster
BK, DAY 28										
Pan #	12.000	14.000	15.000	16.000						
Dry Wt. (g)	0.636	0.650	0.678	0.741						
Spec 480 nm	0.222	0.252	0.075	0.091						
ug INT formazan/g	43.232	47.995	13.699	15.215						
ug INT formazan/g (bl corr.)	40.795	45.558	11.262	12.778						
4S, DAY 27										
Pan #	13.000	14.000	15.000	16.000						
Dry Wt. (g)	0.601	0.833	0.637	0.713						
Spec 480 nm	0.166	0.196	0.115	0.119						
ug INT formazan/g	34.220	29.157	22.377	20.675						
ug INT formazan/g (bl corr.)	24.595	19.532	12.752	11.049						
4D, DAY 27										
Pan #	29.000	30.000	31.000	32.000						
Dry Wt. (g)	0.822	0.593	0.763	0.659						
Spec 480 nm	0.399	0.241	0.340	0.212						
ug INT formazan/g	60.165	50.377	55.228	39.868						
ug INT formazan/g (bl corr.)	55.114	45.326	50.177	34.817						
3D, DAY 27										
Pan #	45.000	46.000	47.000	48.000						
Dry Wt. (g)	0.691	0.596	0.582	0.650						
Spec 480 nm	0.385	0.338	0.621	0.215						
ug INT formazan/g	69.028	70.203	132.129	40.974						
ug INT formazan/g (bl corr.)	57.466	58.642	120.567	29.412						

U.S. EPA Denitrification Study					
Results of microbial enumerations and activity assays					
compiled 11-14-97					
Denitrifiers					
location	log mpn/g	mpn/g			
pr	3.6	4.30E+03			
ccg	5.0	9.30E+04			
cc	4.4	2.30E+04			
ncg	5.7	4.60E+05			
nc	>6.4	> 2.40E+06			
R2A Counts					
location	CFU/gdwt	s.d.	location	log CFU/gdwt	log s.d.
pr	6.10E+05	1.10E+05	pr	5.8	5.0
ccg	5.10E+04	8.40E+03	ccg	4.7	3.9
cc	3.50E+05	1.90E+04	cc	5.5	4.3
ncg	3.50E+05	1.00E+05	ncg	5.5	5.0
nc	1.30E+07	9.60E+05	nc	7.1	6.0
Benzene-Toluene Degraders					
location	log mpn/g	mpn/g			
pr	1.6	4.30E+01			
ccg	2.2	1.50E+02			
cc	2.7	4.60E+02			
ncg	2.4	2.40E+02			
nc	3.9	7.50E+03			
INT Formazan Production - 27 days					
location	INT formazan				
	ug/gdwt				
pr	29.6				
cc	29.4				
ncg	15.1				
nc	62.6				

U.S. EPA DENITRIFICATION STUDY						
INJECTION RATE (ML/MIN)						
Date	Elapsed Time (days)	Measured Injection Rates		Mean Injection Rates		
		Control Cell (ml/min)	Nitrate Cell (ml/min)	Control Cell	Nitrate Cell	
						means for day 1 through 13
21-May-96	35206	7	154	263	154	263
24-May-96	35209	10	231	234	231	234
24-May-96	35209	10	250	250	250	250
28-May-96	35213	14	300	300		
1-Jun-96	35217	18	250	281	mean:	211.7
1-Jun-96	35217	18	300	300	variance:	2584.3
14-Jun-96	35230	31	302	321	n=	3
26-Jun-96	35242	43	284	292		
26-Jun-96	35242	43	300	300	means for day 14 though 66	
29-Jun-96	35245	46	272	272	300	300
2-Jul-96	35248	49	268	272	250	281
9-Jul-96	35255	56	265	281	300	300
9-Jul-96	35255	56	287	295	302	321
20-Jul-96	35266	67	200	200	284	292
22-Jul-96	35268	69	214	218	300	300
5-Aug-96	35282	83	220	196	272	272
5-Aug-96	35282	83	250	230	268	272
14-Aug-96	35291	92	207	207	265	281
21-Aug-96	35298	99	218	218	287	295
4-Sep-96	35312	113	207	203		
4-Sep-96	35312	113	226	210	mean:	282.8
13-Oct-96	35351	152	198	210	variance:	333.7
						n= 10
			245.6	252.4		
			41.2	40.6	means for day 67 though 152	
						200
						200
						214
						218
						220
						196
						250
						230
						207
						207
						218
						218
						207
						203
						226
						210
						198
						210
						mean:
						215.6
						210.2
						variance:
						252.5
						110.2
						n=
						9
						overall
						mean
						236.7
						250.2
						pooled
						variance
						536.4
						184.1
						pooled
						std. dev.
						23.2
						13.6
						95% C.I.
						11.07
						6.48

U.S. EPA Denitrification Study				
Dissolved Oxygen Data				
Nitrate Cell Injection and Extraction Concentrations				
24 hour mean injection concentrations				
		Elapsed	Influent	Effluent
Date		Pumping Time	Concentration	Concentration
		(days)	(mg/L)	(mg/L)
15-May-96	35200	1	10	0.57
16-May-96	35201	2	9.4	
17-May-96	35202	3	8.3	0.55
19-May-96	35204	5	6.9	
21-May-96	35206	7	7.6	
22-May-96	35207	8	0.48	
25-May-96	35210	11	1.68	
28-May-96	35213	14	0.92	
29-May-96	35214	15	3.10	
29-May-96	35214	15	3.30	
30-May-96	35215	16	3.40	
2-Jun-96	35218	19	3.88	
3-Jun-96	35219	20	2.22	
4-Jun-96	35220	21	1.3	
5-Jun-96	35221	22	1.1	
7-Jun-96	35223	24	1.5	
8-Jun-96	35224	25	2.2	
11-Jun-96	35227	28	1.5	
12-Jun-96	35228	29	2.9	
14-Jun-96	35230	31	2.8	
15-Jun-96	35231	32	2.3	
17-Jun-96	35233	34	1	
19-Jun-96	35235	36	2.17	
22-Jun-96	35238	39	1.85	
24-Jun-96	35240	41	0.8	
25-Jun-96	35241	42	2.1	
26-Jun-96	35242	43	2.35	
28-Jun-96	35244	45	1.5	
29-Jun-96	35245	46	2.4	
1-Jul-96	35247	48	2.2	
2-Jul-96	35248	49	2.1	
5-Jul-96	35251	52	2.8	0.38
8-Jul-96	35254	55	2.7	
9-Jul-96	35255	56	1.7	
12-Jul-96	35258	59	3.1	
14-Jul-96	35260	61	2.1	
16-Jul-96	35262	63	1.2	
18-Jul-96	35264	65	1.1	
22-Jul-96	35268	69	1	
23-Jul-96	35269	70	1.95	0.2
24-Jul-96	35270	71	1.3	
29-Jul-96	35275	76	3.8	
31-Jul-96	35277	78	2.9	
1-Aug-96	35278	79	2.5	
4-Aug-96	35281	82	4.1	
5-Aug-96	35282	83	1.7	
10-Aug-96	35287	88	2.9	0.3
14-Aug-96	35291	92	2.5	

U.S. EPA - Denitrification Study		Vertical Profile Data, Post gasoline release		Nitrate Cell		Aromatic hydrocarbon detection limits, given in text									
date	sample	location	depth (cm)	benzene (mg/L)	toluene (mg/L)	ethylbenzene (mg/L)	p,m-xylene (mg/L)	o-xylene (mg/L)	1,3,5-TMB (mg/L)	1,2,4-TMB (mg/L)	1,2,3-TMB (mg/L)	naph (mg/L)	total (mg/L)		
LOCATION: PZ4A															
22-Nov-95	E-41	PZ4A-2	60	32.542	45.813	5.682	12.528	5.328	0.483	1.664	0.440	0.807	105.287		
22-Nov-95	E-42	PZ4A-3	90	35.648	49.934	6.495	14.004	5.943	0.579	1.863	0.518	0.870	115.974		
22-Nov-95	E-43	PZ4A-4	120	27.480	46.135	6.227	13.412	5.661	0.520	1.765	0.469	0.868	102.355		
22-Nov-95	E-44	PZ4A-5	150	3.704	16.544	3.187	6.914	2.761	0.399	1.214	0.312	0.424	35.458		
22-Nov-95	E-45	PZ4A-6	180	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.010		
22-Nov-95	E-46	PZ4A-7	210	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.009		
22-Nov-95	E-47	PZ4A-8	240	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
22-Nov-95	E-48	PZ4A-9	270	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
LOCATION: PZ4B															
22-Nov-95	E-49	PZ4B-2	60	27.689	49.123	6.138	15.048	6.386	0.572	1.990	0.525	0.838	108.308		
22-Nov-95	E-50	PZ4B-3	90	28.693	50.430	7.138	16.720	7.138	0.712	2.444	0.643	0.852	115.279		
22-Nov-95	E-51	PZ4B-4	120	14.108	31.304	4.598	10.003	4.145	0.386	1.333	0.356	0.468	66.708		
22-Nov-95	E-52	PZ4B-5	150	2.575	10.261	1.762	3.778	1.547	0.154	0.475	0.133	0.174	20.891		
22-Nov-95	E-53	PZ4B-6	180	0.091	0.131	0.018	0.048	0.020	0.000	0.000	0.000	0.000	0.309		
22-Nov-95	E-54	PZ4B-7	210	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
22-Nov-95	E-55	PZ4B-8	240	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
22-Nov-95	E-56	PZ4B-9	270	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
LOCATION: PZ4C															
22-Nov-95	E-57	PZ4C-2	60	33.855	54.469	6.977	15.458	6.529	0.617	2.082	0.542	0.918	121.447		
22-Nov-95	E-58	PZ4C-3	90	31.378	50.869	7.042	15.207	6.329	0.777	2.448	0.619	1.161	115.830		
22-Nov-95	E-59	PZ4C-4	120	17.417	33.908	4.506	9.716	4.071	0.395	1.315	0.349	0.457	72.132		
22-Nov-95	E-60	PZ4C-5	150	0.145	1.201	0.322	0.711	0.276	0.045	0.110	0.028	0.000	2.838		
22-Nov-95	E-61	PZ4C-6	180	0.046	0.019	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.068		
22-Nov-95	E-62	PZ4C-7	210	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
22-Nov-95	E-63	PZ4C-8	240	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
22-Nov-95	E-64	PZ4C-9	270	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007		
LOCATION: PZ4D															
26-Nov-95	E-65	PZ4D-2	60	54.583	67.816	13.781	28.595	11.099	2.971	7.811	1.866	2.510	191.053		
26-Nov-95	E-66	PZ4D-3	90	140.088	185.414	117.321	132.581	64.516	81.035	64.279	15.426	18.290	816.948		
26-Nov-95	E-67	PZ4D-4	120	135.302	208.612	68.376	116.471	53.609	65.179	53.158	13.242	12.774	724.922		
26-Nov-95	E-68	PZ4D-5	150	0.040	0.159	0.088	0.296	0.084	0.170	0.068	0.186	0.042	1.093		
26-Nov-95	E-69	PZ4D-6	180	0.078	0.057	0.027	0.084	0.023	0.017	0.030	0.000	0.000	0.288		
26-Nov-95	E-70	PZ4D-7	210	0.000	0.044	0.137	0.333	0.135	0.175	0.196	0.037	0.000	1.017		
26-Nov-95	E-71	PZ4D-8	240	0.000	0.015	0.046	0.133	0.060	0.052	0.112	0.025	0.000	0.442		
26-Nov-95	E-72	PZ4D-9	270	0.000	0.021	0.085	0.225	0.104	0.038	0.160	0.037	0.014	0.684		

U.S. EPA - Denitrification Study												
Vertical Profile Data, Post gasoline release												
Nitrate Cell												
Aromatic hydrocarbon detection limits given in text												
LOCATION: PZ4E												
28-Nov-95 E-73	PZ4E-2	60	22.268	32.421	4.028	8.919	4.260	0.434	3.668	0.449	1.261	77.706
28-Nov-95 E-74	PZ4E-3	90	lots + lots + lots									
28-Nov-95 E-75	PZ4E-5	150	67.328	92.099	32.596	54.655	21.827	25.222	22.231	5.820	5.630	327.206
28-Nov-95 E-76	PZ4E-6	180	0.059	1.623	1.108	2.511	1.018	0.207	0.605	0.157	0.185	7.472
28-Nov-95 E-77	PZ4E-7	210	0.011	0.057	0.018	0.044	0.018	0.000	0.000	0.000	0.000	0.147
28-Nov-95 E-78	PZ4E-8	240	0.005	0.221	0.232	0.527	0.191	0.063	0.138	0.027	0.000	1.405
28-Nov-95 E-80	PZ4E-9	270	0.068	0.615	0.346	0.742	0.255	0.081	0.183	0.043	0.018	2.352

US EPA DENITRIFICATION STUDY									
NITRATE CELL									
ALL PORTS AT LEVEL -2 (60 CM DEPTH)									
All concentrations in mg/L									
LOCATION PZ4A-2									
Compound	Sample ID:	E-41	E-127	E-188	E-241	E-269	E-310	E-355	E-392
	Date:	22-Nov-95	26-Apr-96	17-May-96	30-May-96	4-Jun-96	12-Jun-96	24-Jun-96	3-Jul-96
Benzene		32.542	30.959	59.901	29.352	19.508	42.992	16.334	3.217
Toluene		45.813	51.294	125.973	57.061	41.437	83.903	56.631	49.407
Ethylbenzene		5.682	6.491	42.479	13.004	7.544	25.718	9.159	7.607
p,m-xylene		12.528	13.844	96.635	27.28	15.893	53.643	19.017	15.928
o-xylene		5.328	5.745	33.711	10.755	6.378	18.978	7.701	6.821
1,3,5-trimethylbenzene		0.483	0.559	13.758	2.848	1.329	6.72	1.316	0.807
1,2,4-trimethylbenzene		1.664	1.88	34.578	7.646	3.715	17.683	3.726	2.486
1,2,3-trimethylbenzene		0.44	0.524	8.308	1.723	0.928	4.481	0.884	0.634
naphthalene		0.807	0.897	6.1	1.435	0.759	3.815	1.249	0.92
total btxtmb		105.287	112.193	421.443	151.102	97.489	257.913	116.017	87.827
NITRATE				0.76	139	143	150	132	144
NITRITE				0.05	1.84	2.83	0.34	1.11	0.1
Dissolved Oxygen				4.7	3.4	0.54	0.37	0.5	1.08
Bromide									
Total Iron						0.05			0.06
Sulfate						6.6			3.1
LOCATION PZ4B-2									
Compound	Sample ID:	E-49	E-136	E-189	E-243		E-312	E-357	
	Date:	22-Nov-95	26-Apr-96	17-May-96	30-May-96		12-Jun-96	24-Jun-96	
Benzene		27.689	29.636	5.891	5.49		3.831	2.004	
Toluene		49.123	56.897	36.056	27.402		35.175	43.992	
Ethylbenzene		6.138	7.41	6.819	4.992		5.598	7.978	
p,m-xylene		15.048	16.106	14.19	10.615		12.083	16.980	
o-xylene		6.388	6.813	5.583	4.437		5.164	7.268	
1,3,5-trimethylbenzene		0.572	0.594	1.122	0.53		0.482	0.696	
1,2,4-trimethylbenzene		1.99	2.098	2.806	1.665		1.574	2.244	
1,2,3-trimethylbenzene		0.525	0.561	0.748	0.46		0.439	0.612	
naphthalene		0.836	0.739	0.731	0.55		0.557	0.971	
total btxtmb		108.309	120.854	73.946	56.141		64.903	82.745	
NITRATE				3.38	151		129	153	
NITRITE				<0.05	0.41		0.06	0.2	
Dissolved oxygen				5.9	3		0.61	0.51	
Bromide									
LOCATION PZ4C-2									
Compound	Sample ID:	E-57	E-145	E-190	E-245		E-314	E-359	
	Date:	22-Nov-95	26-Apr-96	17-May-96	30-May-96		12-Jun-96	24-Jun-96	
Benzene		33.855	44.586	2.57	0.513		0.337	0.470	
Toluene		54.469	80.923	24.056	2.428		2.203	5.353	
Ethylbenzene		6.977	21.482	4.886	1.382		0.495	1.508	
p,m-xylene		15.458	43.354	10.434	3.997		2.224	4.863	
o-xylene		6.529	15.06	4.326	1.337		0.793	1.990	
1,3,5-trimethylbenzene		0.817	5.648	0.585	0.635		0.419	0.616	
1,2,4-trimethylbenzene		2.082	12.507	1.661	1.796		1.099	1.692	
1,2,3-trimethylbenzene		0.542	3.128	0.478	0.413		0.244	0.385	
naphthalene		0.918	2.952	0.495	0.267		0.000	0.327	
total btxtmb		121.447	229.64	49.491	12.766		7.814	17.204	
NITRATE				17.9	139		127	0.2	
NITRITE				<0.05	0.05		0.06	0.2	
Dissolved Oxygen				5.5	2.4		0.71	0.91	
Bromide									

US EPA DENITRIFICATION STUDY									
NITRATE CELL									
ALL PORTS AT LEVEL -2 (60 CM)									
All concentrations in mg/L									
LOCATION PZ4A-2									
Compound	E-426	E-452	E-485	E-521	E-557	E-592	E-659	E-686	
	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	25-Sep-96	16-Oct-96	4-Nov-96	
Benzene	4.223	5.437	7.018	4.337	2.819	0.374		0.37	0.259
Toluene	45.933	51.107	38.991	36.499	31.852	21.781		7.476	2.47
Ethylbenzene	10.061	9.475	7.475	8.003	6.92	7.755		6.652	5.494
p,m-xylene	21.223	20.474	16.150	17.808	15.548	19.28		18.823	16.645
o-xylene	8.745	8.904	7.068	7.606	6.644	8.078		7.579	6.669
1,3,5-trimethylbenzene	1.824	0.845	0.593	0.706	0.583	0.734		0.71	0.707
1,2,4-trimethylbenzene	5.189	2.785	2.032	2.444	2.048	2.574		2.48	2.386
1,2,3-trimethylbenzene	1.272	0.825	0.608	0.694	0.589	0.736		0.709	0.633
naphthalene	1.287	1.119	0.975	1.035	0.939	0.978		1.027	0.981
total btextmb	99.757	100.971	80.91	79.132	67.942	62.29		45.826	36.244
NITRATE	140	33.4	17.3	79.8	94.4	87.8		88.2	118
NITRITE	1.06	2.4	12.2	0.2	0.2	0.2		0.2	0.13
Dissolved Oxygen	0.9	0.81	1.1	0.54	1.12	0.82		0.7	0.95
Bromide									276
Total Iron									
Sulfate									
LOCATION PZ4B-2									
Compound	E-427	E-455	E-488	E-524	E-560	E-595	E-662	E-689	
	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	25-Sep-96	16-Oct-96	4-Nov-96	
Benzene	0.653	0.532	0.466	0.491	0.419	0.447		0.474	0.441
Toluene	5.831	1.728	0.555	0.656	1.259	0.179		0.1	0.03
Ethylbenzene	6.033	2.286	0.853	0.56	0.32	0.27		0.063	0.044
p,m-xylene	14.875	9.265	6.076	4.539	3.227	2.83		0.73	0.269
o-xylene	5.466	2.808	1.918	1.385	1.123	0.854		0.223	0.078
1,3,5-trimethylbenzene	0.728	0.982	0.997	1.027	0.839	0.929		0.825	0.573
1,2,4-trimethylbenzene	2.511	3.261	3.198	3.26	2.493	2.489		1.935	1.046
1,2,3-trimethylbenzene	0.674	0.941	0.850	0.775	0.553	0.522		0.386	0.165
naphthalene	0.944	0.822	0.510	0.283	0.248	0.117		0.108	0.067
total btextmb	37.713	22.625	15.423	12.976	10.481	8.637		4.844	2.713
NITRATE	142	82.4	85.1	75.1	95.2	91.4		92.5	110
NITRITE	0.27	0.2	0.22	0.2	0.2	0.2		0.2	0.14
Dissolved oxygen	0.98	0.78	1.25	0.48	0.75	0.72		0.62	0.87
Bromide									261
LOCATION PZ4C-2									
Compound	E-428	E-458	E-491	E-527	E-563	E-598	E-665	E-692	
	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	25-Sep-96	16-Oct-96	4-Nov-96	
Benzene	0.719	0.431	0.375	0.361	0.368	0.435		0.402	0.331
Toluene	5.594	1.085	0.461	0.35	0.225	0.129		0.04	0.071
Ethylbenzene	1.702	1.709	0.818	0.319	0.259	0.235		0.213	0.303
p,m-xylene	5.266	6.274	3.699	1.664	1.418	1.344		1.177	1.403
o-xylene	2.108	2.084	1.018	0.455	0.42	0.37		0.307	0.377
1,3,5-trimethylbenzene	0.539	0.584	0.610	0.649	0.54	0.581		0.553	0.564
1,2,4-trimethylbenzene	1.503	1.711	1.867	1.843	1.478	1.516		1.413	1.418
1,2,3-trimethylbenzene	0.341	0.479	0.512	0.422	0.313	0.318		0.298	0.276
naphthalene	0.324	0.413	0.295	0.128	0.151	0.102		0.211	0.168
total btextmb	18.096	14.77	9.653	6.189	5.172	5.03		4.614	4.911
NITRATE	138	83.4	88.9	86.5	90.9	88.9		84.4	116
NITRITE	0.54	0.24	0.46	0.34	0.32	0.2		0.28	1.71
Dissolved Oxygen	0.83	0.77	0.83	0.44	0.7	0.83		0.51	0.48
Bromide									267

US EPA DENITRIFICATION STUDY						
NITRATE CELL						
ALL PORTS AT LEVEL -2 (60 CM)						
All concentrations in mg/L						
LOCATION PZ4A-2						
Compound	E-713	E-726	E-740	E-771	E-781	E-798
	4-Dec-96	20-Jan-97	22-Mar-97	26-May-97	12-Jun-97	18-Jul-97
Benzene	0.53	0.427	0.471	0.27	0.338	0.314
Toluene	2.932	3.044	3.425	1.627	1.875	1.953
Ethylbenzene	6.158	6.248	6.45	3.861	3.88	3.857
p,m-xylene	18.443	18.631	19.209	13.34	13.261	12.889
o-xylene	7.37	7.338	7.515	4.774	4.734	4.669
1,3,5-trimethylbenzene	0.738	0.773	0.781	0.649	0.689	0.63
1,2,4-trimethylbenzene	2.666	2.7	2.725	2.368	2.465	2.265
1,2,3-trimethylbenzene	0.726	0.733	0.738	0.653	0.673	0.623
naphthalene	1.044	0.919	1.026	0.91	0.892	0.821
total btxmb	40.607	40.811	42.34	28.452	28.807	28.021
NITRATE	104	94.5	77.2	123	80.2	48.5
NITRITE	1.44	0.66	0.79	0.05	0.05	0.09
Dissolved Oxygen	1.32		1.26	0.57	0.11	0.14
Bromide	264	277	242	65	63	63.4
Total Iron						
Sulfate						
LOCATION PZ4B-2						
Compound						
Benzene						
Toluene						
Ethylbenzene						
p,m-xylene						
o-xylene						
1,3,5-trimethylbenzene						
1,2,4-trimethylbenzene						
1,2,3-trimethylbenzene						
naphthalene						
total btxmb						
NITRATE						
NITRITE						
Dissolved oxygen						
Bromide						
LOCATION PZ4C-2						
Compound	E-716	E-729	E-743			
	4-Dec-96	20-Jan-97	22-Mar-97			
Benzene	0.578	0.462	0.462			
Toluene	0.102	0.136	0.199			
Ethylbenzene	0.374	0.448	0.559			
p,m-xylene	1.662	1.849	2.188			
o-xylene	0.452	0.5	0.591			
1,3,5-trimethylbenzene	0.569	0.578	0.601			
1,2,4-trimethylbenzene	1.535	1.495	1.602			
1,2,3-trimethylbenzene	0.316	0.306	0.33			
naphthalene	0.177	0.049	0.168			
total btxmb	5.765	5.821	6.7			
NITRATE	98.6	96	77			
NITRITE	1.21	0.2	0.49			
Dissolved Oxygen	0.82		1.27			
Bromide	245	252	191			

US EPA DENITRIFICATION STUDY									
NITRATE CELL									
ALL PORTS AT LEVEL -2 (60 CM DEPTH)									
All concentrations in mg/L									
LOCATION PZ4D-2									
Compound	Sample ID:	E-65	E-154	E-191	E-247	E-316	E-361		
	Date:	22-Nov-95	28-Apr-96	17-May-96	30-May-96	12-Jun-96	24-Jun-96		
Benzene		54.583	58.24	59.099	45.381	5.647	2.388		
Toluene		67.816	105.2	126.59	142.768	31.451	20.016		
Ethylbenzene		13.781	32.649	42.292	55.805	11.945	10.808		
p,m-xylene		28.595	64.414	95.891	114.917	24.932	23.245		
o-xylene		11.099	22.407	33.492	40.233	10.109	9.529		
1,3,5-trimethylbenzene		2.971	8.982	13.51	16.108	2.663	1.722		
1,2,4-trimethylbenzene		7.811	20.363	34.054	39.202	6.967	5.260		
1,2,3-trimethylbenzene		1.886	5.025	8.182	9.673	1.771	1.342		
naphthalene		2.51	4.515	6.088	5.522	1.347	1.812		
total btextmb		191.052	321.795	419.196	469.589	96.832	76.122		
NITRATE				10.1	148	132	55.8		
NITRITE				<0.05	0.05	0.32	1.5		
Dissolved Oxygen					6.4	0.74			
Bromide									
LOCATION PZ4E-2									
Compound	Sample ID:	E-73	E-163	E-192	E-249	E-274	E-318	E-363	E-397
	Date:	22-Nov-95	28-Apr-96	17-May-96	30-May-96	4-Jun-96	12-Jun-96	24-Jun-96	3-Jul-96
	Elapsed Time (days)	-174	-18	3	16	21	29	41	50
Benzene		22.268	29.564	16.216	2.502	1.084	0.974	3.366	0.467
Toluene		32.421	50.791	41.102	31.256	27.737	19.463	26.897	25.203
Ethylbenzene		4.028	6.658	8.946	5.624	4.832	5.807	11.701	7.59
p,m-xylene		8.919	14.171	18.408	11.976	10.295	12.458	24.473	16.075
o-xylene		4.26	5.967	6.833	5.013	4.435	5.239	9.776	7.109
1,3,5-trimethylbenzene		0.434	0.848	1.822	0.761	0.438	0.726	2.187	0.614
1,2,4-trimethylbenzene		3.666	2.265	4.666	2.271	1.379	2.122	6.230	2.141
1,2,3-trimethylbenzene		0.449	0.566	1.212	0.81	0.388	0.603	1.529	0.57
naphthalene		1.261	0.955	1.167	0.715	0.512	0.684	1.573	0.894
total btextmb		77.706	111.585	100.37	60.728	51.1	48.078	87.732	60.663
NITRATE				14.5	141	119	128	140	147
NITRITE				0.05	0.05	0.48	0.2	0.37	0.1
Dissolved Oxygen				3.6	5.2	2.04	0.95	1.65	1.57
Bromide									
Total Iron						0.05			0.12
Sulfate						9.47			3.13

US EPA DENITRIFICATION STUDY									
NITRATE CELL									
ALL PORTS AT LEVEL -2 (60 CM)									
All concentrations in mg/L									
LOCATION PZ4D-2									
Compound	E-429	E-461	E-494	E-530	E-566	E-601		E-668	E-695
	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	25-Sep-96		16-Oct-96	4-Nov-96
Benzene	8.109	4.758	1.205	0.575	0.696	0.525		0.388	0.416
Toluene	30.047	20.613	25.477	17.458	11.117	8.796		4.442	4.439
Ethylbenzene	15.316	8.589	8.066	7.865	6.5	6.918		5.759	5.173
p,m-xylene	32.055	18.81	18.143	19.894	15.948	18.387		16.762	15.521
o-xylene	12.555	7.715	7.215	7.281	6.085	7.111		6.421	5.868
1,3,5-trimethylbenzene	3.254	0.772	0.759	0.908	0.727	0.87		0.781	0.863
1,2,4-trimethylbenzene	8.658	2.535	2.568	3.152	2.52	2.999		2.733	2.867
1,2,3-trimethylbenzene	2.093	0.751	0.764	0.895	0.718	0.858		0.787	0.724
naphthalene	2.083	0.985	1.106	1.27	1.023	1.134		1.098	0.976
total btextmb	114.17	65.528	65.303	59.298	45.332	47.578		39.169	36.845
NITRATE	137	80.6	84.3	75.8	79.2	80.8		83.4	95.6
NITRITE	0.94	0.2	0.38	3.33	0.73	0.2		0.2	0.19
Dissolved Oxygen	0.97	1.24	0.43	0.5	0.55	0.57		0.49	0.42
Bromide									234
LOCATION PZ4E-2									
Compound	E-430	E-464	E-497	E-533	E-569	E-604	E-617	E-671	E-698
	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	25-Sep-96	2-Oct-96	16-Oct-96	4-Nov-96
	56	70	84	99	113	134	141	155	174
Benzene	1.112	1.146	leaked	0.507	0.473	0.459	0.459	0.403	0.373
Toluene	15.282	4.318		1.128	1.629	1.028	0.627	0.983	0.624
Ethylbenzene	8.308	4.82		1.157	1.247	1.202	1.062	2.258	2.619
p,m-xylene	17.936	14.177		5.75	4.832	5.142	4.745	8.518	9.947
o-xylene	7.684	4.682		1.741	1.700	1.826	1.730	3.092	3.756
1,3,5-trimethylbenzene	0.775	0.851		1.182	0.884	1.072	0.909	0.939	0.855
1,2,4-trimethylbenzene	2.551	2.811		3.847	2.702	3.072	2.554	2.775	2.541
1,2,3-trimethylbenzene	0.684	0.846		0.933	0.620	0.674	0.554	0.674	0.593
naphthalene	1.033	1.091		0.458	0.286	0.199	0.130	0.585	0.683
total btextmb	55.325	34.742		16.703	14.373	14.674	12.77	20.227	21.991
NITRATE	145	76.4	64.4	85.3	92.1	89.1	106	84	113
NITRITE	0.88	0.25	0.46	0.44	0.22	0.28	0.12	0.2	0.18
Dissolved Oxygen	1.13	1.68	0.43	0.37	0.95	0.53	0.45	0.78	0.35
Bromide									257
Total Iron				0.05			0.05		
Sulfate				7.88			8.27		

US EPA DENITRIFICATION STUD)						
NITRATE CELL						
ALL PORTS AT LEVEL -2 (60 CM						
All concentrations in mg/L						
LOCATION PZ4D-2						
Compound						
Benzene						
Toluene						
Ethylbenzene						
p,m-xylene						
o-xylene						
1,3,5-trimethylbenzene						
1,2,4-trimethylbenzene						
1,2,3-trimethylbenzene						
naphthalene						
total btextmb						
NITRATE						
NITRITE						
Dissolved Oxygen						
Bromide						
LOCATION PZ4E-2						
Compound	E-719	E-732	E-746	E-774	E-784	E-801
	4-Dec-96	20-Jan-97	22-Mar-97	26-May-97	12-Jun-97	18-Jul-97
	204	251	312	377	394	430
Benzene	0.583	0.452	0.486	0.254	0.36	0.315
Toluene	0.411	0.388	0.395	0.128	0.149	0.136
Ethylbenzene	2.612	2.485	2.433	1.528	1.497	1.286
p,m-xylene	10.132	9.804	9.707	7.131	7.049	6.063
o-xylene	3.809	3.623	3.562	2.446	2.395	2.047
1,3,5-trimethylbenzene	0.821	0.808	0.825	0.741	0.796	0.657
1,2,4-trimethylbenzene	2.592	2.479	2.499	2.385	2.519	2.086
1,2,3-trimethylbenzene	0.663	0.602	0.622	0.622	0.655	0.49
naphthalene	0.675	0.493	0.581	0.349	0.374	0.367
total btextmb	22.296	21.134	21.11	15.582	15.794	13.447
NITRATE	102	85	67.8	97.6	41.3	51.4
NITRITE	0.23	0.2	0.09	0.7	0.05	0.05
Dissolved Oxygen	0.72		0.48	0.82	0.15	0.44
Bromide	255	282	257	67.4	65.1	65.1
Total Iron			0.12		0.61	
Sulfate			1.97		3.61	

US EPA DENITRIFICATION STUDY									
NITRATE CELL									
ALL PORTS AT LEVEL -6 (180 CM)									
All concentrations in mg/L									
LOCATION PZ4A-6									
Compound	Sample ID:	E-45	E-131	E-231	E-285	E-300	E-345	E-388	E-416
	Date:	22-Nov-95	26-Apr-96	30-May-96	4-Jun-96	12-Jun-96	24-Jun-96	3-Jul-96	9-Jul-96
	Elapsed Time (days)	-174	-18	18	21	29	41	50	56
Benzene		0.000	0.000	17.338	17.788	13.357	20.730	9.408	2.734
Toluene		0.000	0.000	30.422	29.984	21.384	43.672	53.309	51.841
Ethylbenzene		0.000	0.000	3.968	3.932	2.428	5.856	6.971	6.782
p,m-xylene		0.000	0.000	8.526	8.308	5.030	12.302	14.589	14.278
o-xylene		0.000	0.000	3.616	3.536	2.003	5.266	6.407	6.273
1,3,5-trimethylbenzene		0.000	0.000	0.348	0.319	0.132	0.522	0.551	0.529
1,2,4-trimethylbenzene		0.000	0.000	1.131	1.054	0.346	1.624	1.902	1.808
1,2,3-trimethylbenzene		0.000	0.000	0.31	0.290	0.065	0.450	0.501	0.484
naphthalene		0.000	0.000	0.382	0.366	0.325	0.675	0.763	0.75
TOTAL BTEXTMB		0.000	0.000	66.051	65.585	45.070	91.097	94.409	85.485
NITRATE				47.3	12.7	71	14.7	143	130
NITRITE				1.99	2.54	17.2	5.17	0.32	0.56
Dissolved Oxygen				0.44		0.82	0.22	1.05	0.79
Bromide									
Total Iron						0.05		0.09	
Sulfate						6.6		2.64	
LOCATION PZ4B-6									
Compound	Sample ID:	E-53	E-140	E-233		E-302	E-347		E-418
	Date:	22-Nov-95	26-Apr-96	30-May-96		12-Jun-96	24-Jun-96		9-Jul-96
Benzene		0.091	0.000	16.613		7.382	7.560		0.783
Toluene		0.131	0.000	32.814		33.302	56.936		49.731
Ethylbenzene		0.018	0.000	0.419		4.263	7.360		7.141
p,m-xylene		0.048	0.000	8.920		9.072	15.561		15.145
o-xylene		0.020	0.000	3.806		3.931	6.672		6.638
1,3,5-trimethylbenzene		0.000	0.000	0.342		0.336	0.619		0.584
1,2,4-trimethylbenzene		0.000	0.000	1.118		1.099	1.960		2.024
1,2,3-trimethylbenzene		0.000	0.000	0.309		0.309	0.542		0.541
naphthalene		0.000	0.000	0.407		0.395	0.852		0.817
TOTAL BTEXTMB		0.308	0.000	64.748		60.089	98.082		83.404
NITRATE				122		122	149		144
NITRITE				0.61		0.67	0.22		0.84
Dissolved Oxygen				1.62		0.95	0.51		1.35
Bromide									
LOCATION PZ4C-6									
Compound	Sample ID:	E-61	E-149	E-235		E-304	E-349		E-420
	Date:	22-Nov-95	26-Apr-96	30-May-96		12-Jun-96	24-Jun-96		9-Jul-96
Benzene		0.048	0.000	2.926		1.029	1.290		0.707
Toluene		0.019	0.000	33.434		32.341	48.011		27.552
Ethylbenzene		0.000	0.000	4.281		4.372	7.807		7.68
p,m-xylene		0.000	0.000	9.101		9.353	16.337		16.268
o-xylene		0.000	0.000	3.894		4.012	7.022		7.175
1,3,5-trimethylbenzene		0.000	0.000	0.353		0.354	0.641		0.601
1,2,4-trimethylbenzene		0.000	0.000	1.171		1.157	2.036		2.032
1,2,3-trimethylbenzene		0.000	0.000	0.324		0.321	0.567		0.559
naphthalene		0.000	0.000	0.390		0.407	0.912		0.865
TOTAL BTEXTMB		0.065	0.000	55.874		53.346	84.623		63.439
NITRATE				132		151	139		128
NITRITE				0.18		0.26	0.57		0.83
Dissolved Oxygen				0.72		0.83	0.6		0.84
Bromide									
LOCATION PZ4D-6									
Compound	Sample ID:	E-69	E-158	E-237		E-306	E-351		E-422
	Date:	26-Nov-95	26-Apr-96	30-May-96		12-Jun-96	24-Jun-96		9-Jul-96
Benzene		0.078	0.062	18.648		17.075	16.285		29.816
Toluene		0.057	0.118	28.123		31.757	56.065		48.109
Ethylbenzene		0.027	0.000	3.820		4.034	7.140		6.240
p,m-xylene		0.064	0.000	8.129		8.558	14.922		13.021
o-xylene		0.023	0.000	3.378		3.645	6.413		5.681
1,3,5-trimethylbenzene		0.017	0.000	0.322		0.339	0.579		0.491
1,2,4-trimethylbenzene		0.030	0.000	1.053		1.090	1.864		1.695
1,2,3-trimethylbenzene		0.000	0.000	0.290		0.306	0.515		0.455
naphthalene		0.000	0.000	0.381		0.388	0.789		0.695
TOTAL BTEXTMB		0.298	0.180	64.144		67.192	104.552		106.203
NITRATE				140		127	131		124
NITRITE				0.71		0.5	0.43		1.3
Dissolved Oxygen				0.76		0.44	0.99		0.92
Bromide									

US EPA DENITRIFICATION STUDY								
NITRATE CELL								
ALL PORTS AT LEVEL -6 (180 CI)								
All concentrations in mg/L								
LOCATION PZ4A-6								
Compound	E-453	E-486	E-522	E-558	E-593	E-660	E-687	E-714
	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	25-Sep-96	16-Oct-96	4-Nov-96	4-Dec-96
Benzene	70	84	99	113	134	155	174	204
Toluene	13,964	19,867	14,516	8,199	1,824	0,305	0,194	0,436
Ethylbenzene	65,168	57,729	51,523	48,967	52,47	28,037	5,361	1,654
Ethylbenzene	8,425	7,063	7,032	6,149	7,32	7,837	7,632	6,499
p,m-xylene	17,753	15,035	14,976	13,072	15,69	16,72	16,556	16,515
o-xylene	7,695	6,612	6,387	5,678	6,746	7,211	6,848	6,013
1,3,5-trimethylbenzene	0,703	0,555	0,585	0,481	0,588	0,605	0,613	0,661
1,2,4-trimethylbenzene	2,332	1,881	2,029	1,692	2,047	2,115	2,075	2,458
1,2,3-trimethylbenzene	0,668	0,568	0,585	0,485	0,584	0,617	0,546	0,684
naphthalene	0,964	0,834	0,824	0,742	0,792	0,886	0,874	1
TOTAL BTEXTMB	117,672	110,144	98,457	85,465	88,061	64,333	40,696	35,940
NITRATE	133	26.9	40.2	32.1	90.5	95.2	94	21.8
NITRITE	1.37	9.32	3.21	0.8	0.95	0.22	0.19	1.78
Dissolved Oxygen	0.91	1.58	0.47				0.9	0.84
Bromide							249	128
Total Iron								
Sulfate								
LOCATION PZ4B-6								
Compound	E-456	E-489	E-525	E-561	E-596	E-663	E-690	
	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	25-Sep-96	16-Oct-96	4-Nov-96	
Benzene	0,000	0,742	0,328	0,358	0,363	0,369	0,267	
Toluene	26,375	23,382	4,602	6,969	13,879	0,19	0,065	
Ethylbenzene	8,365	8,251	8,734	7,885	8,493	7,528	4,917	
p,m-xylene	17,756	17,492	18,765	18,896	18,461	18,307	15,307	
o-xylene	7,735	7,692	8,023	7,276	7,81	6,654	3,705	
1,3,5-trimethylbenzene	2,224	0,652	0,665	0,622	0,708	0,708	0,725	
1,2,4-trimethylbenzene	2,216	2,206	2,467	2,181	2,462	2,472	2,459	
1,2,3-trimethylbenzene	0,655	0,670	0,716	0,624	0,703	0,707	0,655	
naphthalene	0,933	0,982	1,026	0,979	0,966	1,063	1,068	
TOTAL BTEXTMB	66,259	62,069	45,348	43,792	53,665	37,998	29,168	
NITRATE	153	89.4	90.4	89.2	89.8	85.8	105	
NITRITE	0.32	0.67	0.86	0.2	0.56	0.26	0.15	
Dissolved Oxygen	1.02	1.09	0.89				1.39	
Bromide							256	
LOCATION PZ4C-6								
Compound	E-459	E-492	E-528	E-564	E-599	E-666	E-693	E-717
	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	25-Sep-96	16-Oct-96	4-Nov-96	4-Dec-96
Benzene	0,541	0,364	0,331	0,306	0,35	0,345	0,206	0,401
Toluene	21,709	12,825	7,045	1,38	2,971	0,566	0,907	0,605
Ethylbenzene	8,332	7,903	8,41	7,074	7,958	7,267	6,898	4,591
p,m-xylene	17,592	17,016	18,181	15,759	18,091	17,666	16,11	10,519
o-xylene	7,739	7,369	7,757	6,147	6,897	5,652	5,475	3,808
1,3,5-trimethylbenzene	0,875	0,642	0,671	0,554	0,679	0,677	0,658	0,485
1,2,4-trimethylbenzene	2,239	2,147	2,408	1,948	2,389	2,384	2,231	1,707
1,2,3-trimethylbenzene	0,663	0,650	0,681	0,563	0,691	0,692	0,591	0,452
naphthalene	0,916	1,028	0,971	0,871	1,019	1,132	1,02	0,731
TOTAL BTEXTMB	60,406	49,944	46,455	34,602	41,045	36,361	34,096	23,299
NITRATE	136	56.7	90.6	84.1	92.9	95	76.8	15.2
NITRITE	0.2	2.36	0.57	0.43	0.2	0.2	0.57	0.05
Dissolved Oxygen	0.67	0.79	0.81				0.48	0.55
Bromide							124	12.7
LOCATION PZ4D-6								
Compound	E-462	E-495	E-531	E-567	E-602	E-669	E-696	
	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	25-Sep-96	16-Oct-96	4-Nov-96	
Benzene	12,525	leaked	0,684	3,238	7,35	6,763	11,183	
Toluene	53,396		44,426	47,622	48,44	46,167	53,325	
Ethylbenzene	6,683		7,898	6,228	6,725	6,109	7,076	
p,m-xylene	14,017		17,059	13,449	14,734	13,52	15,227	
o-xylene	6,107		7,306	5,725	6,235	5,708	6,516	
1,3,5-trimethylbenzene	0,531		0,731	0,552	0,592	0,554	0,713	
1,2,4-trimethylbenzene	1,771		2,552	1,914	2,066	1,919	2,348	
1,2,3-trimethylbenzene	0,527		0,725	0,545	0,592	0,546	0,595	
naphthalene	0,803		0,97	0,871	0,817	0,829	0,912	
TOTAL BTEXTMB	96,362		82,351	80,144	87,551	82,135	97,895	
NITRATE	140	67.7	85.9	80	89.6	89.8	81.7	
NITRITE	0.55	7.9	0.71	1.32	0.43	0.66	0.25	
Dissolved Oxygen	0.71	0.54	0.84				0.82	
Bromide							0.2	

US EPA DENITRIFICATION STUDY						
NITRATE CELL						
ALL PORTS AT LEVEL -6 (180 CI)						
All concentrations in mg/L						
LOCATION PZ4A-6						
Compound	E-727	E-741	E-772	E-782	E-789	
	20-Jan-97	22-Mar-97	26-May-97	12-Jun-97	18-Jul-97	
Benzene	251	312	377	394	430	
Toluene	0.354	0.357	0.368	0.105	0.116	
Ethylbenzene	2.408	5.117	3.07	0.56	0.284	
Ethylbenzene	5.847	6.588	8.829	2.417	1.588	
p,m-xylene	14.158	18.183	19.218	5.607	3.375	
o-xylene	5.277	6.111	6.134	2.274	1.458	
1,3,5-trimethylbenzene	0.818	0.691	0.695	0.218	0.158	
1,2,4-trimethylbenzene	2.147	2.41	2.479	0.866	0.598	
1,2,3-trimethylbenzene	0.585	0.656	0.672	0.22	0.139	
naphthalene	0.78	0.973	1.002	0.23	0.17	
TOTAL BTEXTMB	31.948	39.086	44.483	12.495	7.884	
NITRATE	4.8	4.5	91.6	23.8	18.7	
NITRITE	0.21	0.05	0.2	0.05	0.63	
Dissolved Oxygen		1.09	0.59	0.09	0.4	
Bromide	90.8	100	64.7	19.3	17.2	
Total Iron						
Sulfate						
LOCATION PZ4B-6						
Compound						
Benzene						
Toluene						
Ethylbenzene						
p,m-xylene						
o-xylene						
1,3,5-trimethylbenzene						
1,2,4-trimethylbenzene						
1,2,3-trimethylbenzene						
naphthalene						
TOTAL BTEXTMB						
NITRATE						
NITRITE						
Dissolved Oxygen						
Bromide						
LOCATION PZ4C-6						
Compound	E-730	E-744				
	20-Jan-97	22-Mar-97				
Benzene	0.118	0.293				
Toluene	0.348	0.481				
Ethylbenzene	3.417	3.832				
p,m-xylene	7.876	9.028				
o-xylene	2.914	3.158				
1,3,5-trimethylbenzene	0.283	0.408				
1,2,4-trimethylbenzene	0.969	1.406				
1,2,3-trimethylbenzene	0.278	0.376				
naphthalene	0.281	0.687				
TOTAL BTEXTMB	16.46	19.669				
NITRATE	2.33	0.29				
NITRITE	0.2	0.05				
Dissolved Oxygen		1.05				
Bromide	7.3	31.1				
LOCATION PZ4D-6						
Compound						
Benzene						
Toluene						
Ethylbenzene						
p,m-xylene						
o-xylene						
1,3,5-trimethylbenzene						
1,2,4-trimethylbenzene						
1,2,3-trimethylbenzene						
naphthalene						
TOTAL BTEXTMB						
NITRATE						
NITRITE						
Dissolved Oxygen						
Bromide						

US EPA DENITRIFICATION STUDY													
NITRATE CELL													
INJECTION AND EXTRACTION PORTS													
Aromatic hydrocarbon detection limits given in text.													
All concentrations in mg/L													
LOCATION: INJECTION PORT													
Compound	Sample ID:	E-179	E-182	E-195	E-207	E-208	E-251	E-277	E-279	E-322	E-324	E-366	E-368
	Date:	15-May-96	17-May-96	21-May-96	25-May-96	29-May-96	1-Jun-96	4-Jun-96	7-Jun-96	12-Jun-96	17-Jun-96	24-Jun-96	29-Jun-96
Benzene		0.000		0.016				0.028					0.000
Toluene		0.000		0.026				0.065					0.000
Ethylbenzene		0.000		0.000				0.000					0.000
p,m-xylene		0.000		0.000				0.000					0.000
o-xylene		0.000		0.000				0.000					0.000
1,3,5-trimethylbenzene		0.000		0.000				0.000					0.000
1,2,4-trimethylbenzene		0.000		0.000				0.000					0.000
1,2,3-trimethylbenzene		0.000		0.000				0.000					0.000
naphthalene		0.000		0.000				0.000					0.000
	Date:	15-May-96	17-May-96	21-May-96	25-May-96	29-May-96	1-Jun-96	4-Jun-96	7-Jun-96	12-Jun-96	17-Jun-96	24-Jun-96	29-Jun-96
NITRATE		121.0	123.0	136.0	148.0	144	151	0.05	183	134	155	141	
NITRITE		0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.24	0.2	0.2	0.2	
TOTAL FE								0.05					
SULFATE								2					
BROMIDE													
Note: injection samples E-195 and E-277 collected from end of injection tubing which was submerged in contaminated injection well.													
These samples not representative of supply water.													
LOCATION: EXTRACTION PORT													
Compound	Sample ID:	pw4-1	pw4-2	pw4-3	pw4-1	pw4-2	pw4-3	pw4-1	pw4-2	pw4-3	pw4-1	pw4-2	pw4-3
	Date:	25-Mar-96	25-Mar-96	25-Mar-96	3-Apr-96	3-Apr-96	3-Apr-96	6-Apr-96	6-Apr-96	6-Apr-96	15-Apr-96	15-Apr-96	15-Apr-96
	Elapsed Time (days)												
Benzene		8.014	0.573	3.392	0.796	5.26	6.261	1.421	6.147	6.87	0.869	4.692	6.04
Toluene		17.465	2.568	8.098	1.76	12.616	13.868	3.435	14.339	15.886	2.916	10.771	14.317
Ethylbenzene		3.962	0.75	1.376	0.354	1.877	2.004	0.554	2.12	2.354	0.485	1.588	2.142
p,m-xylene		8.051	1.581	2.82	0.751	3.753	4.116	1.121	4.369	4.779	0.984	3.273	4.473
o-xylene		2.957	0.591	1.122	0.293	1.518	1.656	0.456	1.78	1.968	0.402	1.325	1.8
1,3,5-trimethylbenzene		0.788	0.117	0.147	0.098	0.195	0.21	0.108	0.208	0.224	0.102	0.16	0.202
1,2,4-trimethylbenzene		2.029	0.314	0.424	0.191	0.524	0.551	0.233	0.58	0.625	0.212	0.437	0.587
1,2,3-trimethylbenzene		0.517	0.087	0.122	0.038	0.145	0.161	0.05	0.166	0.179	0.044	0.121	0.169
naphthalene		0.603	0.091	0.145	0.038	0.206	0.205	0.038	0.213	0.284	0	0.193	0.176
TOTAL BTEXTMB		44.366	6.672	17.646	4.319	26.094	29.032	7.416	29.922	33.169	6.014	22.56	29.906
NITRATE													
NITRITE													
TOTAL FE													
SULFATE													

US EPA DENITRIFICATION STUDY														
NITRATE CELL														
INJECTION AND EXTRACTION PORTS														
Aromatic hydrocarbon detection limits														
All concentrations in mg/L														
LOCATION: INJECTION PORT														
Compound	E-369	E-400	E-433	E-434	E-469	E-502	E-540	E-574	E-575	E-576	E-609	E-622	E-674	E-678
	28-Jun-96	3-Jul-96	9-Jul-96	16-Jul-96	29-Jul-96	6-Aug-96	3-Jul-96	4-Sep-96	9-Sep-96	9-Sep-96	#####	2-Oct-96	16-Oct-96	21-Oct-96
Benzene	0.000					0.000	0.000					0.000		
Toluene	0.000					0.000	0.000					0.011		
Ethylbenzene	0.000					0.000	0.000					0.000		
p,m-xylene	0.000					0.000	0.000					0.000		
o-xylene	0.000					0.000	0.000					0.000		
1,3,5-trimethylbenzene	0.000					0.000	0.000					0.000		
1,2,4-trimethylbenzene	0.000					0.000	0.000					0.000		
1,2,3-trimethylbenzene	0.000					0.000	0.000					0.000		
naphthalene	0.000					0.000	0.000					0.000		
NITRATE	28-Jun-96	3-Jul-96	9-Jul-96	16-Jul-96	29-Jul-96	6-Aug-96	3-Jul-96	4-Sep-96	9-Sep-96	9-Sep-96	#####	2-Oct-96	16-Oct-96	21-Oct-96
		146	175	158	86.3	83.3	83.5	83.5	97.6	91.6	93.7	108	97.7	98.3
NITRITE		0.1	0.43	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
TOTAL FE		0.18					0.12	0.12	0.12	0.12	0.17	0.17	0.17	0.2
SULFATE		2.4					7.67	7.67	7.67	7.67	8.52	8.52	8.52	8.52
BROMIDE														
LOCATION: EXTRACTION PORT														
Compound	E-177	E-181	E-186	E-278	E-321	E-367	E-399	E-432	E-468	E-501	E-539	E-573	E-610	E-623
	15-May-96	17-May-96	21-May-96	4-Jun-96	12-Jun-96	24-Jun-96	3-Jul-96	9-Jul-96	23-Jul-96	6-Aug-96	#####	4-Sep-96	#####	2-Oct-96
Benzene	6.225	9.528	12.961	12.478	10.393	12.576	11.538	11.538	9.147	6.358	6.1	2.875	2.355	1.994
Toluene	11.471	17.09	21.602	26.131	26.616	39.95	39.821	36.835	35.493	34.589	28.801	28.01	33.731	29.093
Ethylbenzene	1.552	2.288	2.678	3.239	3.693	5.359	5.609	5.578	5.985	5.71	6.703	6.15	6.947	5.753
p,m-xylene	3.293	5.193	5.642	6.746	7.814	11.217	11.689	11.714	12.638	11.945	14.361	13.18	14.989	12.427
o-xylene	1.368	1.996	2.32	2.921	3.415	4.878	5.2	5.189	5.551	5.399	6.122	5.611	6.368	5.240
1,3,5-trimethylbenzene	0.175	0.224	0.227	0.266	0.301	0.427	0.441	0.424	0.465	0.421	0.514	0.449	0.54	0.432
1,2,4-trimethylbenzene	0.435	0.639	0.643	0.828	1.01	1.439	1.501	1.461	1.502	1.402	1.762	1.595	1.91	1.524
1,2,3-trimethylbenzene	0.134	0.184	0.197	0.237	0.281	0.389	0.405	0.399	0.399	0.457	0.528	0.467	0.56	0.444
naphthalene	0.162	0.223	0.257	0.287	0.372	0.594	0.618	0.608	0.651	0.717	0.761	0.743	0.818	0.552
TOTAL BTEX/TMB	24.815	37.373	48.548	53.131	55.885	76.828	76.822	71.355	69.101	66.722	62.527	58.58	68.138	57.459
NITRATE	0.05	38.10	39.60	89	112	70.8	120	115	115	46.3	69	73	80.6	85.7
NITRITE	0.05	0.05	0.84	1.83	1.49	3.34	nd	1.95	1.74	4.9	1.27	0.63	0.76	0.63
TOTAL FE				0.27	0.27						6.56			0.15
SULFATE														8.54

US EPA DENITRIFICATION STUDY									
NITRATE CELL									
INJECTION AND EXTRACTION PORTS									
Aromatic hydrocarbon detection limits									
All concentrations in mg/L									
LOCATION: INJECTION PORT									
Compound	E-678A 28-Oct-96	E-679 28-Oct-96	E-685 28-Oct-96	E-761 6-May-97	E-763 9-May-97	E-766 9-May-97	E-767 17-May-97	E-768 26-May-97	
Benzene									
Toluene									
Ethylbenzene									
p,m-xylene									
o-xylene									
1,3,5-trimethylbenzene									
1,2,4-trimethylbenzene									
1,2,3-trimethylbenzene									
naphthalene									
	28-Oct-96								
NITRATE	114			126	123	114	99.9	119	
NITRITE	0.2			0.05	0.05	0.05	0.05	0.05	
TOTAL FE		0.22	0.29						
SULFATE		2.08							
BROMIDE				273	229	224	60.2	74.6	
Note: E-685 unfiltered sample for iron									
LOCATION: EXTRACTION PORT									
Compound	E-675 16-Oct-96	E-681 28-Oct-96	E-701 4-Nov-96	E-757 2-May-97	E-764 9-May-97	E-769 26-May-97	mean for May 1997		
							mean	s.d	
Benzene	155		174	175	182	199	199	0.5	0.044
Toluene	0.931		0.608	0.543	0.54	0.466	0.54	0.5	1.284
Ethylbenzene	25.734		19.108	18.635	21.099	19.24	19.7	5.2	0.084
p,m-xylene	6.007		5.182	5.126	5.278	5.262	5.2	4.6	0.161
o-xylene	13.276		11.702	11.473	11.847	11.794	11.6	0.034	0.023
1,3,5-trimethylbenzene	5.439		4.667	4.595	4.579	4.53	4.6	0.084	0.021
1,2,4-trimethylbenzene	0.485		0.51	0.457	0.43	0.475	0.5	0.4	0.158
1,2,3-trimethylbenzene	1.705		1.728	1.6	1.549	1.713	1.6	44.7	1.226
naphthalene	0.498		0.692	0.595	0.359	0.658	0.5		
TOTAL BTEXIMB	54.836		44.648	43.483	45.913	44.809	44.7		
NITRATE	767		77.1	59.2	232	64.9	118.7		
NITRITE	0.61		1.91	0.62	0.12	0.84	4.2		
TOTAL FE		0.22							
SULFATE		3.92							

U.S. EPA - Denitrification Study								
Vertical Profile Data								
Nitrate Cell								
All concentrations in mg/L.								
date	date	elapsed time (days)	sample	location	depth (cm)	benzene	toluene	ethylbenze
LOCATION: PZ4E								
26-Apr-96	35181	-18	E-162	PZ4E-1	30	24.44	62.346	11.344
26-Apr-96	35181	-18	E-163	PZ4E-2	60	29.564	50.791	6.658
26-Apr-96	35181	-18	E-164	PZ4E-3	90	73.906	162.872	63.302
26-Apr-96	35181	-18	E-165	PZ4E-5	150	42.546	72.171	18.005
26-Apr-96	35181	-18	E-166	PZ4E-6	180	0.155	1.352	0.277
26-Apr-96	35181	-18	E-167	PZ4E-7	210	0.018	0.101	0
26-Apr-96	35181	-18	E-168	PZ4E-8	240	0.062	0.108	0.021
26-Apr-96	35181	-18	E-169	PZ4E-9	270	0.086	0.159	0.034
4-Jun-96	35220	21	E-274	PZ4E-2	60	1.084	27.737	4.832
4-Jun-96	35220	21	E-273	PZ4E-3	90	297.783	684.877	283.637
4-Jun-96	35220	21	E-272	PZ4E-5	150	36.715	58.397	15.56
4-Jun-96	35220	21	E-271	PZ4E-6	180	21.381	31.621	4.03
4-Jun-96	35220	21	E-270	PZ4E-7	210	17.903	25.611	2.604
3-Jul-96	35249	50	E-397	PZ4E-2	60	0.467	25.203	7.59
3-Jul-96	35249	50	E-396	PZ4E-3	90	11.787	59.961	15.637
3-Jul-96	35249	50	E-395	PZ4E-5	150	31.283	50.688	9.597
3-Jul-96	35249	50	E-394	PZ4E-6	180	30.489	48.575	6.222
3-Jul-96	35249	50	E-393	PZ4E-7	210	25.798	46.084	5.382
21-Aug-96	35298	99	E-533	PZ4E-2	60	0.507	1.128	1.157
21-Aug-96	35298	99	E-534	PZ4E-3	90	1.059	35.671	7.128
21-Aug-96	35298	99	E-535	PZ4E-5	150	9.355	56.994	7.556
21-Aug-96	35298	99	E-536	PZ4E-6	180	11.553	55.13	7.315
21-Aug-96	35298	99	E-537	PZ4E-7	210	1.015	0.188	0.456
2-Oct-96	35340	141	E-617	PZ4E-2	60	0.459	0.627	1.082
2-Oct-96	35340	141	E-618	PZ4E-3	90	1.029	24.725	7.602
2-Oct-96	35340	141	E-619	PZ4E-5	150	7.082	49.370	8.403
2-Oct-96	35340	141	E-620	PZ4E-6	180	4.882	48.871	6.267
2-Oct-96	35340	141	E-621	PZ4E-7	210	14.292	48.606	6.040
18-Jul-97	35629	430	E-812	PZ4E-1	30	0.019	0.143	0.039
18-Jul-97	35629	430	E-801	PZ4E-2	60	0.315	0.136	1.286
18-Jul-97	35629	430	E-802	PZ4E-3	90	1.173	9.004	7.770
18-Jul-97	35629	430	E-803	PZ4E-5	150	1.784	47.976	6.202
18-Jul-97	35629	430	E-804	PZ4E-6	180	0.373	13.439	2.576
18-Jul-97	35629	430	E-805	PZ4E-7	210	0.596	27.208	5.358

U.S. EPA - Denitrification Stu							
Vertical Profile Data							
Nitrate Cell							
All concentrations in mg/L.							
date	p,m-xylene	o-xylene	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB	naph	TOTAL
LOCATION: PZ4E							
26-Apr-96	24.092	9.63	1.84	5.259	1.318	1.655	141.924
26-Apr-96	14.171	5.967	0.648	2.265	0.566	0.955	111.585
26-Apr-96	146.775	49.275	19.175	54.461	12.949	10.135	592.85
26-Apr-96	35.526	12.667	4.262	10.06	2.522	2.28	200.039
26-Apr-96	0.583	0.238	0.041	0.146	0	0	2.792
26-Apr-96	0.061	0	0	0	0	0	0.18
26-Apr-96	0.048	0.018	0	0.027	0	0	0.284
26-Apr-96	0.073	0.03	0	0.05	0	0	0.432
4-Jun-96	10.295	4.435	0.438	1.379	0.388	0.512	51.1
4-Jun-96	570.743	201.291	5.063	215.72	50.612	9.235	2318.961
4-Jun-96	31.861	11.881	3.711	9.541	0.703	1.843	170.212
4-Jun-96	8.462	3.59	0.34	1.128	0.309	0.414	71.275
4-Jun-96	5.247	2.347	0.063	0.209	0.069	0.065	54.118
3-Jul-96	16.075	7.109	0.614	2.141	0.57	0.894	60.663
3-Jul-96	31.482	12.208	3.654	9.833	2.295	2.176	149.033
3-Jul-96	19.41	7.875	1.803	5.054	1.197	1.162	128.049
3-Jul-96	12.937	5.717	0.502	1.735	0.459	0.689	107.325
3-Jul-96	10.998	4.872	0.27	0.998	0.279	0.356	95.037
21-Aug-96	5.75	1.741	1.182	3.847	0.933	0.458	16.703
21-Aug-96	15.222	6.554	0.612	2.128	0.613	0.913	69.9
21-Aug-96	16.5	6.954	0.632	2.207	0.623	0.851	101.672
21-Aug-96	15.541	6.605	0.6	2.052	0.591	0.789	100.176
21-Aug-96	0.965	0.413	0.03	0.106	0.031	0.038	3.242
2-Oct-96	4.745	1.730	0.909	2.554	0.554	0.130	12.77
2-Oct-96	16.103	7.014	0.596	2.073	0.590	0.800	60.532
2-Oct-96	14.332	6.116	0.553	1.923	0.547	0.714	87.04
2-Oct-96	13.248	5.682	0.505	1.757	0.502	0.653	82.365
2-Oct-96	12.774	5.512	0.422	1.510	0.440	0.517	90.113
18-Jul-97	0.199	0.099	0.041	0.080	0.032	0.041	0.693
18-Jul-97	6.036	2.047	0.657	2.088	0.490	0.367	13.42
18-Jul-97	16.168	7.010	0.587	2.088	0.569	0.868	45.237
18-Jul-97	13.158	5.548	0.447	1.760	0.429	0.693	77.997
18-Jul-97	5.365	2.155	0.230	0.864	0.201	0.232	25.435
18-Jul-97	11.493	4.906	0.331	1.347	0.336	0.361	51.936

U.S. EPA - Denitrification Study					
Vertical Profile Data					
Nitrate Cell					
All concentrations in mg/L.					
date	NITRATE	NITRITE	D.O.	TOT. FE	SULFATE
LOCATION: PZ4E					
26-Apr-96					
4-Jun-96	119	0.48	2.04	0.05	9.47
4-Jun-96	138	0.2		0.05	7.73
4-Jun-96	160	1.49	0.97	0.07	8.94
4-Jun-96	77.5	0.2	0.51	0.05	5.79
4-Jun-96	53.1	4.16	0.92	0.515	26.5
3-Jul-96	147	0.1	1.57	0.12	3.13
3-Jul-96	140	0.25	1.21	0.05	3.38
3-Jul-96	137	1.61	0.91	0.09	3.81
3-Jul-96	150	0.18	1.34	0.07	2.66
3-Jul-96	36.6	5.01	0.74	0.55	7.94
21-Aug-96	85.3	0.44	0.37	0.05	7.88
21-Aug-96	82.7	1		0.05	7.45
21-Aug-96	86.3	1.68		0.05	7.66
21-Aug-96	90.5	1.05	0.49	0.05	7.63
21-Aug-96	41.0	1.4		0.15	6.22
2-Oct-96	106	0.12	0.45	0.05	8.27
2-Oct-96	101	0.88	1.08		
2-Oct-96	101	2.24	0.86		
2-Oct-96	107	0.15	0.72		
2-Oct-96	90.5	0.52	0.95	0.26	8.46
18-Jul-97			1.060		
18-Jul-97	51.4	0.05	0.44		
18-Jul-97			0.41		
18-Jul-97			0.49		
18-Jul-97	90.4	0.6	0.33		
18-Jul-97	11.1	0.05	0.24		

U.S. EPA Deminification Study													
Nitrate Cell													
Core extract samples													
Zeros used for not-detected samples													
Method detection limits provided in text.													
Core 4H													
Depth Interval: 0.155													
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)		
0.1	138	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.8	
0.2	139	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	23.3	
0.4	140	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	38.8	
0.5	141	11.7	50.3	23.5	68.7	17.4	77.7	188.4	34.9	15.6	486.2	54.3	
0.7	142	21.3	76.4	282.4	635.0	173.1	104.1	281.9	64.0	64.8	1682.9	69.8	
0.8	143	14.2	55.1	226.7	496.5	183.3	71.2	193.5	42.8	41.1	1327.3	85.3	
1.0	144	18.0	215.3	278.2	609.0	222.0	86.1	234.1	52.5	50.6	1766.7	100.8	
1.2	145	0.0	0.0	0.0	3.3	0.0	0.0	0.0	0.0	0.0	3.3	116.3	
	g/m2	21.7	132.3	264.8	603.4	198.6	113.0	298.2	64.7	57.3	1755.0		
Core 4I													
Depth Interval: 0.155													
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)		
0.1	130	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.8	
0.2	131	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	23.3	
0.4	132	10.1	94.6	53.3	153.5	46.7	54.8	133.7	28.6	25.0	600.5	38.8	
0.5	133	17.5	187.1	237.0	528.6	190.8	76.1	203.8	45.6	48.2	1534.6	54.3	
0.7	134	19.0	543.0	288.7	635.1	228.2	92.5	251.3	55.0	53.3	2187.3	68.8	
0.8	135	0.0	66.4	27.1	59.3	21.4	10.2	23.5	5.1	4.9	217.9	85.3	
1.0	136	0.0	6.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.9	100.8	
1.2	137	0.0	7.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.4	116.3	
	g/m2	15.5	301.8	202.0	458.7	182.7	77.8	204.1	44.8	43.8	1511.1		
Core 4J													
Depth Interval: 0.144													
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)		
0.1	163	0.0	0.0	0.0	8.0	3.0	0.0	4.4	0.0	0.0	15.4	7.2	
0.2	164	0.0	10.1	4.0	18.5	6.7	4.6	9.8	0.0	0.0	53.7	21.6	
0.4	165	0.0	0.0	0.0	3.9	0.0	0.0	0.0	0.0	0.0	3.9	38.0	
0.5	166	15.6	213.8	230.4	582.2	210.1	80.6	218.3	49.1	47.8	1648.0	50.4	
0.6	167	22.1	698.3	338.0	734.3	285.5	109.5	292.8	65.6	63.4	2580.4	64.8	
0.8	168	11.0	421.0	170.7	375.1	135.6	58.0	150.4	33.4	31.5	1384.6	79.2	
0.9	169	18.9	705.8	284.3	621.9	224.6	93.3	248.0	55.8	51.6	2306.1	93.6	
1.1	170	0.0	22.0	6.6	15.1	5.8	0.0	5.8	0.0	0.0	55.2	108.0	
1.2	171	0.0	10.5	0.0	5.3	0.0	0.0	0.0	0.0	0.0	15.9	122.4	
	g/m2	21.2	644.4	320.5	732.0	263.5	106.5	288.3	63.2	60.1	2488.7		

U.S. EPA Denitrification Study												
Nitrate Cell												
Core extract samples												
Zeroes used for not-detected samples												
Method detection limits provided in text.												
Core 4K	Depth Interval: 0.145											
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
0.0725	13	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.3
0.2175	14	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21.6
0.3625	15	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	36.3
0.5075	16	17.3	71.0	35.6	181.0	42.3	108.7	279.5	56.3	27.8	820.7	50.8
0.8525	17	21.0	79.3	322.6	760.1	237.6	290.7	65.1	67.0	74.5	1951.4	65.3
0.7975	18	24.2	267.7	389.3	848.1	312.1	121.9	326.7	73.3	68.4	2437.8	79.8
0.9425	19	23.5	633.8	353.8	774.2	279.0	115.6	311.3	69.9	68.4	2828.6	94.3
1.0875	20	33.5	1293.5	537.3	1161.1	431.8	184.6	504.3	114.6	134.5	4415.5	108.8
1.5925	21	0.0	6.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.2	159.3
1.7375	22	0.0	3.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.8	173.8
1.8825	23	0.0	0.0	0.0	3.6	0.0	0.0	0.0	0.0	0.0	3.6	188.3
2.0275	24	0.0	4.7	5.2	12.8	5.2	0.0	3.1	0.0	0.0	30.9	202.6
	g/m2	50.2	1301.1	720.5	1628.5	574.9	271.1	730.0	162.6	168.1	5607.9	
Core 4L	Depth Interval: 0.145											
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
0.0725	146	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.3
0.2175	147	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21.6
0.3625	148	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	36.3
0.5075	149	38.0	258.6	72.6	282.5	75.5	233.9	518.2	110.8	67.7	1638.1	50.8
0.8525	150	20.1	62.1	60.9	257.0	67.3	91.4	258.4	56.9	44.7	938.9	65.3
0.7975	151	20.9	90.4	331.9	723.9	288.8	101.3	273.7	62.0	59.4	1832.2	79.8
0.9425	152	20.7	184.2	275.0	600.3	219.5	86.3	231.9	51.9	50.3	1720.1	94.3
1.0875	153	45.4	1602.5	650.3	1423.0	515.1	215.9	575.9	128.0	126.8	5283.8	108.8

U.S. EPA Denitrification Study										
Water content data from multilevel TDR probes, Nitrate Cell										
Gasoline spills on October 16 (Control Cell) and October 17 (Nitrate Cell)										
C4U8					C4U5					
Depth (cm)	17-Oct-95 (%)	17-Oct-95 (Saturation)	18-Oct-95 (%)	20-Oct-95 (%)	1-Nov-95 (%)	29-Feb-96 (%)	Depth (m)	Depth (cm)	17-Oct-95 (%)	17-Oct-95 (Saturation)
194.2	20.36	45.31	14.37	15.32	15.47	15.42	1.942	193.7	42.16	95.08
184.2	44.93	100.00	44.84	44.48	43.45	45.9	1.842	183.7	43.83	98.85
174.2	43.7	97.26	43.48	43.39	44.12	45.14	1.742	173.7	43.91	99.03
164.2	44.17	98.31	43.07	43.62	43.81	41.99	1.642	163.7	42.87	96.68
154.2	43.65	97.15	43.6	43.78	43.69	46.06	1.542	153.7	43.75	98.67
144.2	43.39	96.57	42.97	42.94	43.09	44.42	1.442	143.7	44.34	100.00
134.2	41.56	92.50	42.61	43.1	43.28	43.74	1.342	133.7	41.32	93.19
124.2	22.94	51.06	37.62	38.81	41.44	42.53	1.242	123.7	32.87	74.13
114.2	17.15	38.17	21.69	25.02	37.75	40.71	1.142	113.7	17.98	40.55
104.2	15.91	35.41	20.07	29.32	36.92	40.33	1.042	103.7	19.22	43.35
94.2	16.2	36.06	19.72	21.79	35.59	40.31	0.942	93.7	20.39	45.99
84.2	17.32	38.55	17.25	19.3	36.91	39.87	0.842	83.7	20.47	46.17
74.2	17.5	38.95	16.9	18.65	38.51	40.4	0.742	73.7	17.64	39.78
64.2	15.53	34.56	16.4	16.99	30.93	39.46	0.642	63.7	15.39	34.71
54.2	15.88	35.34	13.13	11.95	13.05	47.69	0.542	53.7	13.89	31.33
44.2	25.25	56.20	21.73	20.93	19.86	40.95	0.442	43.7	24.56	55.39
34.2	19.36	43.09	23.04	21.8	20.82	42.27	0.342	33.7	20.28	45.74
24.2	14.37	31.98	15.32	15.47	15.42	38.42	0.242	23.7	13.09	29.52

18-Oct-95 (%)	20-Oct-95 (%)	1-Nov-95 (%)	29-Feb-96 (%)	Depth (m)	17-Oct-95 (%)	17-Oct-95 (Saturation)	18-Oct-95 (%)	20-Oct-95 (%)	1-Nov-95 (%)	29-Feb-96 (%)	Depth (m)
13.09	15.14		14.27	1.937	38.24	85.28	15.38	14.48	13.41	13.85	1.957
43.72	44.48		43.43	1.837	44.02	98.17	45.97	45.1	45.29	48.23	1.857
44.06	44.06		44.68	1.737	44.62	99.51	44.35	44.5	43.57	46.88	1.757
44.1	44.43	44.8	44.67	1.637	44.37	98.95	44.13	44.44	44.79	48.12	1.657
43.63	42.91	44.37	44.2	1.537	43.55	97.12	36.3	40.65	42.25	46.39	1.557
43.46	43.47	43.73	44.91	1.437	44.84	100.00	25.99	37.95	39.97	45	1.457
43.89	43.93	44.27	44.4	1.337	42.77	95.38	20.36	35.16	40.71	46.84	1.357
41.42	41.9	42.12	43.65	1.237	33.27	74.20	24.4	31.85	39.9	47.06	1.257
32.51	36.61	41.68	42.8	1.137	27.37	61.04	26.38	30.59	40.34	45.57	1.157
22	32.68	39.09	40.3	1.037	19.01	42.40	23.74	29.97	37.28	43.71	1.057
22.32	28.04	37.78	43.52	0.937	19.97	44.54	21.47	22.68	36.55	41.44	0.957
21.64	23.61	39.1	42.76	0.837	18.46	41.17	18.71	21.77	36.53	40.97	0.857
19.17	20.6	39.46	40.95	0.737	17.32	38.63	20.24	19.29	37.36	33.65	0.757
16.62	17.65	35.69	40.49	0.637	14.34	31.98	15.79	16.32	29.47	28.19	0.657
12.96	12.87	15.48	42.87	0.537	12.95	28.88	12.38	11.88	11.64	28.82	0.557
19.7	19.05	17.73	38.47	0.437	24.51	54.66	18.49	18.12	17.61	28.88	0.457
21.44	20.3	20.44	41.21	0.337	17.11	38.16	21.62	20.64	19.95	25.71	0.357
15.14	14.48	14.27	38.24	0.237	15.38	34.30	14.48	13.41	13.85	20.36	0.257

C4U1

U.S. EPA Denitrification Study				
Dissolved Oxygen Data				
Control Cell Injection and Extraction Concentrations				
24 hour mean injection concentrations				
Date	Date	Elapsed	Influent	Effluent
		Pumping Time	Concentration	Concentration
		(days)	(mg/L)	(mg/L)
15-May-96	35200	1	8.6	0.17
16-May-96	35201	2	6.7	
17-May-96	35202	3	8.3	0.38
19-May-96	35204	5	7.7	
21-May-96	35206	7	6.2	
22-May-96	35207	8	0.5	0.33
24-May-96	35209	10	0.2	
25-May-96	35210	11	2.14	
28-May-96	35213	14	1.69	
29-May-96	35214	15	2.8	
29-May-96	35214	15	4.3	
30-May-96	35215	16	4.8	
2-Jun-96	35218	19	3.96	
3-Jun-96	35219	20	1.72	
4-Jun-96	35220	21	3.3	1.08
5-Jun-96	35221	22	2.1	
7-Jun-96	35223	24	2.3	
8-Jun-96	35224	25	1.9	
11-Jun-96	35227	28	1.1	
12-Jun-96	35228	29	3.1	
14-Jun-96	35230	31	2.4	
15-Jun-96	35231	32	2.3	
17-Jun-96	35233	34	2.8	
19-Jun-96	35235	36	3.15	
22-Jun-96	35238	39	0.85	
24-Jun-96	35240	41	0.8	
25-Jun-96	35241	42	0.2	
26-Jun-96	35242	43	1.6	
28-Jun-96	35244	45	1.9	
29-Jun-96	35245	46	2.2	
1-Jul-96	35247	48	1.6	
2-Jul-96	35248	49	1.65	
5-Jul-96	35251	52	3	0.3
8-Jul-96	35254	55	1.6	
9-Jul-96	35255	56	1.5	
12-Jul-96	35258	59	3.9	
14-Jul-96	35260	61	2	
16-Jul-96	35262	63	2.15	
18-Jul-96	35264	65	1.3	
22-Jul-96	35268	69	2.5	
23-Jul-96	35269	70	1.5	0.17
24-Jul-96	35270	71	3.1	
29-Jul-96	35275	76	3.4	
31-Jul-96	35277	78	3.1	
1-Aug-96	35278	79	3	
4-Aug-96	35281	82	2.85	
5-Aug-96	35282	83	3.1	

U.S. EPA - Denitification Study Vertical Profile Data, Post gasoline release Control Cell Aromatic hydrocarbon detection limits given in text													
date	sample	location	depth (cm)	benzene (mg/L)	toluene (mg/L)	ethylbenzene (mg/L)	p,m-xylene (mg/L)	o-xylene (mg/L)	1,3,5-TMB (mg/L)	1,2,4-TMB (mg/L)	1,2,3-TMB (mg/L)	naph (mg/L)	total (mg/L)
LOCATION: PZ3A													
22-Nov-95	E-1	PZ3A-2	60	31.104	56.238	7.117	16.725	7.103	0.709	2.403	0.823	1.010	123.031
22-Nov-95	E-2	PZ3A-3	90	28.467	50.814	7.035	15.104	6.397	0.609	2.033	0.542	0.745	112.745
22-Nov-95	E-3	PZ3A-4	120	18.432	41.760	5.743	12.284	5.219	0.454	1.570	0.417	0.687	86.577
22-Nov-95	E-4	PZ3A-5	150	17.636	40.221	5.471	11.757	4.991	0.427	1.416	0.393	0.546	82.857
22-Nov-95	E-5	PZ3A-6	180	0.003	0.058	0.015	0.043	0.015	0.000	0.000	0.000	0.000	0.134
22-Nov-95	E-6	PZ3A-7	210	0.000	0.018	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.018
22-Nov-95	E-7	PZ3A-8	240	0.032	0.038	0.008	0.028	0.000	0.000	0.000	0.000	0.000	0.103
22-Nov-95	E-8	PZ3A-9	270	0.000	0.020	0.011	0.027	0.011	0.000	0.000	0.000	0.000	0.069
LOCATION: PZ3B													
22-Nov-95	E-9	PZ3B-2	60	27.726	61.874	10.322	22.884	9.356	1.715	4.825	1.206	1.611	141.519
22-Nov-95	E-10	PZ3B-3	90	0.188	0.266	0.065	0.140	0.053	0.000	0.000	0.000	0.000	0.711
22-Nov-95	E-11	PZ3B-4	120	0.347	0.302	0.054	0.128	0.047	0.000	0.000	0.000	0.000	0.678
22-Nov-95	E-12	PZ3B-5	150	0.636	0.419	0.144	0.302	0.108	0.000	0.000	0.000	0.000	1.608
22-Nov-95	E-13	PZ3B-6	180	0.006	0.018	0.000	0.019	0.000	0.000	0.000	0.000	0.000	0.043
22-Nov-95	E-14	PZ3B-7	210	NS	NS	NS	NS	NS	NS	NS	NS	NS	0.000
22-Nov-95	E-15	PZ3B-8	240	0.004	0.029	0.012	0.037	0.014	0.000	0.000	0.000	0.000	0.086
22-Nov-95	E-16	PZ3B-9	270	0.006	0.066	0.016	0.067	0.021	0.000	0.000	0.000	0.000	0.181
LOCATION: PZ3C													
22-Nov-95	E-17	PZ3C-2	60	41.974	52.993	6.986	16.152	6.738	0.737	2.398	0.242	0.900	128.131
22-Nov-95	E-18	PZ3C-3	90	3.087	8.841	1.394	3.075	1.264	0.153	0.428	0.119	0.112	18.474
22-Nov-95	E-19	PZ3C-4	120	0.091	0.228	0.141	0.318	0.115	0.047	0.100	0.021	0.000	1.060
22-Nov-95	E-20	PZ3C-5	150	0.000	0.030	0.012	0.034	0.012	0.000	0.000	0.000	0.000	0.088
22-Nov-95	E-21	PZ3C-6	180	0.037	0.024	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.082
22-Nov-95	E-22	PZ3C-7	210	0.000	0.020	0.000	0.029	0.000	0.000	0.000	0.000	0.000	0.049
22-Nov-95	E-23	PZ3C-8	240	0.065	0.078	0.110	0.312	0.108	0.148	0.382	0.094	0.004	1.322
22-Nov-95	E-24	PZ3C-9	270	0.008	1.024	0.750	1.831	0.728	0.187	0.464	0.125	0.103	5.198
LOCATION: PZ3D													
28-Nov-95	E-25	PZ3D-2	60	32.856	51.326	6.448	14.939	6.374	0.724	3.006	0.617	1.066	117.358
28-Nov-95	E-26	PZ3D-3	90	958.751	702.913	560.398	207.048	185.662	313.145	48.678	189.721	51.403	3215.919
28-Nov-95	E-27	PZ3D-4	120	98.697	134.436	31.714	18.136	30.730	33.203	28.524	6.858	7.060	390.358
28-Nov-95	E-28	PZ3D-5	150	10.139	33.862	5.554	12.165	4.831	0.668	1.996	0.508	0.727	70.539
28-Nov-95	E-29	PZ3D-6	180	0.000	0.014	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.014
28-Nov-95	E-30	PZ3D-7	210	0.008	0.038	0.008	0.026	0.000	0.000	0.000	0.000	0.000	0.083
28-Nov-95	E-31	PZ3D-8	240	0.005	0.041	0.016	0.047	0.016	0.000	0.007	0.000	0.000	0.130
28-Nov-95	E-32	PZ3D-9	270	0.291	0.922	0.308	0.659	0.226	0.081	0.190	0.045	0.034	2.757

U.S. EPA - Denitrification Study		Vertical Profile Data, Post gasoline release																		
Control Cell		Aromatic hydrocarbon detection limits given in text																		
LOCATION:	PZ3E																			
26-Nov-95	E-33	PZ3E-2	60	83.482	81.785	20.239	40.482	15.527	14.587	12.779	3.045	3.475	255.371							
26-Nov-95	E-34	PZ3E-3	90	78.657	105.349	32.854	55.136	21.866	7.344	20.677	4.705	5.133	332.750							
26-Nov-95	E-35	PZ3E-4	120	34.951	49.873	6.802	14.170	5.939	0.655	2.118	0.545	1.142	115.994							
26-Nov-95	E-36	PZ3E-5	150	105.976	122.842	45.517	69.783	28.378	31.193	26.945	6.502	6.534	443.670							
26-Nov-95	E-37	PZ3E-6	180	0.039	0.246	0.540	1.246	0.434	0.090	0.260	0.067	0.037	2.958							
26-Nov-95	E-38	PZ3E-7	210	0.007	0.046	0.013	0.036	0.013	0.000	0.000	0.000	0.000	0.118							
26-Nov-95	E-39	PZ3E-8	240	0.005	0.047	0.018	0.049	0.020	0.018	0.000	0.000	0.000	0.156							
26-Nov-95	E-40	PZ3E-9	270	0.008	0.062	0.031	0.080	0.031	0.030	0.070	0.018	0.009	0.340							

US EPA DENITRIFICATION STUDY													
CONTROL CELL													
ALL PORTS AT LEVEL -2 (60 CM DEPTH)													
All concentrations in mg/L													
Compound	Sample ID:	E-1	E-82	E-202	E-221	E-257	E-290	E-335	E-380	E-411	E-437	E-470	E-503
	Date:	22-Nov-95	25-Apr-96	21-May-96	30-May-96	4-Jun-96	12-Jun-96	24-Jun-96	3-Jul-96	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96
LOCATION PZ3A-2													
Benzene		31.104	27.639	9.022	2.977	10.642	0.987	1.139	0.429	0.761	1.082	0.650	0.446
Toluene		56.238	52.743	25.942	11.617	22.602	6.708	10.764	2.762	7.618	11.096	7.906	6.409
Ethylbenzene		7.117	6.901	4.246	2.305	2.189	1.442	2.508	0.944	2.041	2.369	2.369	2.369
p,m-xylene		16.725	14.924	9.142	5.067	4.343	3.26	6.463	2.251	4.803	6.806	5.269	5.44
o-xylene		7.103	6.289	3.685	2.002	1.938	1.278	2.455	0.849	1.9227	2.751	2.152	2.031
1,3,5-trimethylbenzene		0.709	0.583	0.426	0.319	0.078	0.699	1.390	0.490	0.355	0.423	0.354	0.372
1,2,4-trimethylbenzene		2.403	2.046	1.373	0.855	0.264	0.18	0.360	0.145	0.266	0.352	0.298	0.302
1,2,3-trimethylbenzene		0.623	0.553	0.370	0.249	0.080	0.163	0.396	0.146	0.213	0.301	0.307	0.305
naphthalene		1.010	0.845	0.458	0.253	0.055	0.148	0.396	0.146	0.213	0.301	0.307	0.305
TOTAL BTEXTMB		123.032	112.523	54.664	25.744	42.171	14.956	25.956	8.410	19.012	27.041	20.345	18.792
Dissolved Oxygen			0.56		2.2	1.8	1.3	0.58	1.49	0.74	0.83	1.2	1.06
Total Iron						0.07			0.07				
Sulfate						13.8			3.22				
LOCATION PZ3B-2													
Compound	Sample ID:	E-9	E-91	E-203	E-223	E-292	E-337	E-412	E-440	E-473	E-506		
	Date:	22-Nov-95	25-Apr-96	21-May-96	30-May-96	12-Jun-96	24-Jun-96	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96		
Benzene		27.726	26.550	6.504	3.267	1.194	1.194	2.685	1.766	1.231	0.579		
Toluene		61.874	52.425	20.467	12.488	8.072	8.072	27.024	14.895	11.655	7.059		
Ethylbenzene		10.322	9.913	4.101	2.185	1.421	1.421	5.280	4.779	4.347	3.892		
p,m-xylene		22.884	14.595	9.088	4.851	3.518	3.518	11.767	10.775	10.01	9.142		
o-xylene		9.356	6.076	3.567	1.989	1.415	1.415	4.904	3.806	3.436	3.337		
1,3,5-trimethylbenzene		1.716	0.550	0.316	0.316	0.23	0.23	0.550	0.503	0.577	0.588		
1,2,4-trimethylbenzene		4.825	1.821	1.687	0.951	0.661	0.661	1.694	1.656	1.621	1.873		
1,2,3-trimethylbenzene		1.206	0.508	0.434	0.249	0.173	0.173	0.462	0.437	0.519	0.542		
naphthalene		1.611	0.695	0.504	0.282	0.172	0.172	0.710	0.542	0.546	0.595		
TOTAL BTEXTMB		141.519	110.033	46.936	26.556	16.856	16.856	55.076	32.599	39.844	34.822	27.654	
Dissolved Oxygen			0.45		1.9	0.94	0.94	0.54	0.95	1.42	0.49	0.9	
LOCATION PZ3C-2													
Compound	Sample ID:	E-17	E-100	E-204	E-225	E-284	E-339	E-413	E-443	E-476	E-509		
	Date:	22-Nov-95	25-Apr-96	21-May-96	30-May-96	12-Jun-96	24-Jun-96	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96		
Benzene		41.974	29.469	1.014	0.485	0.217	0.217	0.435	0.441	0.358	0.178	0.182	
Toluene		52.993	58.925	5.503	2.492	1.249	1.249	3.136	2.243	4.706	1.978	0.752	
Ethylbenzene		6.996	7.742	1.771	0.937	0.514	0.514	0.845	0.761	1.416	0.768	0.541	
p,m-xylene		18.152	16.873	3.947	2.222	1.255	1.255	2.879	2.546	3.435	1.858	1.25	
o-xylene		6.739	7.159	1.394	0.814	0.457	0.457	1.05	0.923	1.388	0.749	0.44	
1,3,5-trimethylbenzene		0.737	0.63	0.367	2.076	0.159	0.159	0.344	0.324	0.256	0.149	0.146	
1,2,4-trimethylbenzene		2.398	2.198	0.979	0.624	0.425	0.425	0.888	0.928	0.663	0.374	0.339	
1,2,3-trimethylbenzene		0.242	0.589	0.259	0.154	0.102	0.102	0.218	0.216	0.188	0.102	0.1	
naphthalene		0.9	0.753	0.248	0.102	0.076	0.076	0.165	0.176	0.111	0.000	0.011	
TOTAL BTEXTMB		129.131	124.336	15.472	9.908	4.454	4.454	9.96	8.558	12.531	6.174	3.761	
Dissolved Oxygen			0.79		1.2	1.9	1.9	1.81	2.24	0.84	0.78	0.65	

US EPA DENTRIFICATION STUJ		CONTROL CELL		ALL PORTS AT LEVEL -2 (60 CM)		All concentrations in mg/L	
LOCATION	Compound	E-542	E-577	E-644	E-702	E-722	
		4-Sep-96	25-Sep-96	16-Oct-96	4-Nov-96	4-Dec-96	
LOCATION PZ3A-2							
Compound							
Benzene		0.188	0.178	0.158	0.095	0.397	
Toluene		1.794	1.498	1.152	0.487	2.349	
Ethylbenzene		0.563	0.578	0.603	0.378	0.977	
p,m-xylene		1.254	1.442	1.404	0.886	2.163	
o-xylene		0.508	0.566	0.537	0.33	0.835	
1,3,5-trimethylbenzene		0.105	0.128	0.108	0.107	0.198	
1,2,4-trimethylbenzene		0.265	0.335	0.314	0.288	0.578	
1,2,3-trimethylbenzene		0.073	0.08	0.082	0.067	0.133	
naphthalene		0.064	0.068	0.078	0.175	0.198	
TOTAL BTEXTM8		4.814	4.882	4.437	2.833	7.828	
Dissolved Oxygen		0.72	0.99	0.69	1.18		
Total Iron							
Sulfate							
LOCATION PZ3B-2							
Compound							
Benzene		0.355	0.251	0.144	0.082		
Toluene		2.902	1.959	1.085	0.309		
Ethylbenzene		1.433	1.123	0.612	0.308		
p,m-xylene		3.285	2.68	1.430	0.753		
o-xylene		1.248	0.978	0.520	0.252		
1,3,5-trimethylbenzene		0.238	0.239	0.134	0.122		
1,2,4-trimethylbenzene		0.715	0.724	0.403	0.343		
1,2,3-trimethylbenzene		0.194	0.192	0.102	0.073		
naphthalene		0.185	0.128	0.124	0.065		
TOTAL BTEXTM8		10.555	8.274	4.554	2.307		
Dissolved Oxygen		0.68	0.62	0.72	0.94		
LOCATION PZ3C-2							
Compound							
Benzene		0.289	0.354	0.251	0.17		
Toluene		1.752	2.857	1.191	0.727		
Ethylbenzene		1.08	1.408	0.774	0.617		
p,m-xylene		2.523	3.316	1.862	1.472		
o-xylene		0.921	1.219	0.668	0.517		
1,3,5-trimethylbenzene		0.239	0.307	0.205	0.203		
1,2,4-trimethylbenzene		0.708	0.908	0.589	0.561		
1,2,3-trimethylbenzene		0.183	0.235	0.148	0.122		
naphthalene		0.148	0.123	0.199	0.119		
TOTAL BTEXTM8		7.821	10.525	5.863	4.508		
Dissolved Oxygen		0.61	0.78	0.61	0.69		

US EPA DENITRIFICATION STUDY													
CONTROL CELL													
ALL PORTS AT LEVEL -2 (60 CM DEPTH)													
All concentrations in mg/L													
Compound	Sample ID:	E-25	E-109	E-205	E-227	E-283	E-288	E-343	E-386	E-414	E-446	E-479	E-512
	Date:	22-Nov-95	25-Apr-96	21-May-96	30-May-96	4-Jun-96	12-Jun-96	24-Jun-96	3-Jul-96	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96
Benzene		32.856	28.911	1.215	20.964	0.746	0.485	0.228	0.160	0.318	0.127	0.106	0.066
Toluene		51.328	48.785	4.305	40.116	4.909	4.301	2.838	0.803	1.436	1.503	0.900	0.23
Ethylbenzene		6.448	6.061	1.275	8.279	2.132	0.891	0.788	0.338	0.454	0.872	0.531	0.204
p,m-xylene		14.939	13.018	2.712	17.367	4.971	2.04	1.738	0.831	1.261	1.741	1.259	0.487
o-xylene		6.374	5.522	0.971	6.833	1.9	0.838	0.694	0.299	0.458	0.701	0.480	0.171
1,3,5-trimethylbenzene		3.006	1.898	0.605	4.289	0.782	0.194	0.213	0.097	0.189	0.141	0.094	0.064
1,2,4-trimethylbenzene		0.617	0.478	0.171	1.035	0.213	0.55	0.613	0.321	0.092	0.276	0.263	0.107
1,2,3-trimethylbenzene		1.066	0.789	0.147	0.872	0.194	0.157	0.172	0.031	0.116	0.092	0.075	0.034
naphthalene		117.356	106.99	11.637	101.3	19.176	9.599	7.245	2.938	4.812	5.253	3.708	1.483
TOTAL BTEXTMB				0.33	3.3			1.3	1.46	3.0	1.75	0.65	0.57
Dissolved Oxygen													
LOCATION PZ3E-2													
Compound	Sample ID:	E-33	E-118	E-206	E-229	E-283	E-288	E-343	E-386	E-415	E-449	E-482	E-515
	Date:	22-Nov-95	25-Apr-96	21-May-96	30-May-96	4-Jun-96	12-Jun-96	24-Jun-96	3-Jul-96	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96
	Elapsed Time (days)	-174	-18	7	16	21	21	41	50	56	70	84	98
Benzene		63.482	36.932	1.546	0.746	0.485	0.228	2.026	0.160	0.413	0.400	broken	0.222
Toluene		81.795	64.831	7.416	4.909	4.301	2.838	8.614	0.803	1.580	4.227		0.892
Ethylbenzene		20.239	13.162	2.415	2.132	0.891	0.788	4.024	0.338	0.716	2.110		0.774
p,m-xylene		40.482	28.178	5.477	4.971	2.04	1.738	8.545	0.831	1.959	4.664		1.912
o-xylene		15.527	11.402	2.021	1.9	0.838	0.694	2.975	0.299	0.736	1.870		0.827
1,3,5-trimethylbenzene		14.567	3.242	0.513	0.782	0.194	0.213	1.194	0.097	0.230	0.265		0.189
1,2,4-trimethylbenzene		12.779	8.981	1.423	2.255	0.55	0.613	3.187	0.321	0.631	0.657		0.529
1,2,3-trimethylbenzene		3.045	2.174	0.383	0.964	0.145	0.172	0.765	0.031	0.151	0.208		0.153
naphthalene		3.475	2.281	0.406	0.517	0.157	0.163	0.782	0.058	0.000	0.000		0.103
TOTAL BTEXTMB		255.371	172.163	21.6	19.176	9.599	7.245	32.312	2.938	6.416	14.501		5.401
Dissolved Oxygen				1.91	3.9			1.46	0.98	2.4	0.96	0.37	0.46
Total Iron						0.05			0.08				0.05
Sulfate						7.32			3.23				7.65

283

US EPA DENITRIFICATION STU											
CONTROL CELL											
ALL PORTS AT LEVEL -2 (60 CM)											
All concentrations in mg/L											
LOCATION PZ3D-2											
Compound	E-551	E-586		E-653	E-708						
	4-Sep-96	25-Sep-96		16-Oct-96	4-Nov-96						
Benzene	0.131	0.182		0.114	0.07						
Toluene	1.794	2.235		1.305	0.57						
Ethylbenzene	0.867	1.301		0.802	0.507						
p,m-xylene	0.02	3.075		1.860	1.165						
o-xylene	0.802	1.174		0.702	0.428						
1,3,5-trimethylbenzene	0.12	0.196		0.122	0.102						
1,2,4-trimethylbenzene	0.362	0.607		0.383	0.307						
1,2,3-trimethylbenzene	0.099	0.167		0.104	0.066						
naphthalene	0.098	0.079		0.109	0.085						
TOTAL BTEXTMB	4.283	9.018		5.501	3.300						
Dissolved Oxygen	1	0.55		0.61	0.79						
LOCATION PZ3E-2											
Compound	E-554	E-589	E-611	E-656	E-710	E-724	E-735	E-749	E-777	E-787	E-806
	4-Sep-96	25-Sep-96	2-Oct-96	16-Oct-96	4-Nov-96	4-Dec-96	20-Jan-97	22-Mar-97	26-May-97	12-Jun-97	18-Jul-97
	113	134	141	155	174	204	251	312	377	394	430
Benzene	0.097	0.091	0.104	0.021	0.025	0.122	0.203	0.317	0.019	0.111	0.138
Toluene	0.650	0.249	0.354	0.152	0.138	1.045	1.779	4.439	0.03	1.357	2.942
Ethylbenzene	0.192	0.258	0.435	0.088	0.173	0.53	0.839	2.229	0.018	0.693	1.321
p,m-xylene	0.468	0.755	1.101	0.248	0.437	1.211	1.816	4.918	0.054	1.781	3.239
o-xylene	0.193	0.267	0.376	0.088	0.144	0.438	0.665	1.832	0.02	0.668	1.227
1,3,5-trimethylbenzene	0.037	0.083	0.114	0.025	0.053	0.098	0.132	0.281	0.007	0.121	0.194
1,2,4-trimethylbenzene	0.089	0.225	0.329	0.070	0.155	0.298	0.401	0.898	0.021	0.371	0.69
1,2,3-trimethylbenzene	0.028	0.062	0.087	0.019	0.032	0.076	0.101	0.232	0.009	0.113	0.168
naphthalene	0.017	0.000	0.056	0.017	0.121	0.08	0.047	0.217	0.12	0.068	0.128
TOTAL BTEXTMB	1.771	1.99	2.956	0.724	1.278	3.874	5.983	15.383	0.296	5.283	10.047
Dissolved Oxygen	1	0.74	0.99	0.62	0.45	0.69	0.96	0.59	1.7	0.09	0.31
Total Iron			0.05					0.36		0.6	
Sulfate			8.42					2.38		2.12	

US EPA DENITRIFICATION STUDY												
CONTROL CELL												
ALL PORTS AT LEVEL ± (180 CM DEPTH)												
Aromatic hydrocarbon detection limits given in text.												
All concentrations in mg/L												
Compound	Sample ID: E-5	E-86	E-211	E-253	E-280	E-325	E-376	E-401	E-438	E-471	E-504	E-543
	Date: 22-Nov-85	25-Apr-86	30-May-86	4-Jul-86	12-Jun-86	24-Jun-86	3-Jul-86	9-Jul-86	23-Jul-86	6-Aug-86	21-Aug-86	4-Sep-86
Benzene	0.003	2.46	15.519	13.039	8.61	7.028	3.889	2.635	0.789	1.411	1.389	0.894
Toluene	0.058	14.407	30.231	32.894	33.005	56.512	47.921	43.729	40.57	29.168	19.418	15.879
Ethylbenzene	0.015	2.848	3.739	4.108	4.045	7.260	6.658	6.649	6.127	7.683	7.828	6.921
p,m-xylene	0.043	5.93	7.699	8.572	8.529	15.118	14.28	13.925	17.247	16.185	16.6233	14.752
o-xylene	0.015	2.346	3.374	3.669	3.697	6.562	6.284	6.183	7.606	7.113	7.183	6.312
1,3-trimethylbenzene	0	0.244	0.371	0.338	0.318	0.590	0.549	0.515	0.659	0.584	0.814	0.526
1,2,4-trimethylbenzene	0	0.752	1.061	1.098	1.034	1.903	1.898	1.777	2.16	1.979	2.109	1.86
1,2,3-trimethylbenzene	0	0.214	0.338	0.305	0.289	0.552	0.503	0.484	0.654	0.601	0.828	0.541
naphthalene	0	0.243	0.372	0.396	0.383	0.820	0.761	0.715	0.818	0.839	0.878	0.892
TOTAL BTEXTMB	0.134	29.442	62.902	64.417	59.81	96.345	82.953	76.612	78.73	65.661	58.6703	48.577
Dissolved Oxygen			1.25	1.47	0.45	0.67	0.91	1.84	1.09	1.4	0.83	
total fe			0.22									
sulfate			12.8									
Compound	Sample ID: E-13	E-95	E-213	E-282	E-327	E-403	E-441	E-474	E-507	E-546		
	Date: 22-Nov-85	25-Apr-86	30-May-86	12-Jun-86	24-Jun-86	9-Jul-86	23-Jul-86	6-Aug-86	21-Aug-86	4-Sep-86		
Benzene	0.006	0.288	BROKEN	3.827	3.180	2.919	1.512	1.937	1.206	1.924		
Toluene	0.018	0.186		34.941	51.396	27.598	21.686	17.139	17.755	16.728		
Ethylbenzene	0	0.312		4.709	7.813	7.321	6.317	6.742	6.132	6.742		
p,m-xylene	0.019	0.494		10.039	16.298	15.33	17.417	17.630	17.832	15.072		
o-xylene	0	0.243		4.303	7.008	6.81	7.664	7.511	7.108	5.656		
1,3-trimethylbenzene	0	0		0.394	0.645	0.561	0.654	0.638	0.654	0.561		
1,2,4-trimethylbenzene	0	0		1.278	2.090	1.978	2.173	2.176	2.358	1.985		
1,2,3-trimethylbenzene	0	0		0.357	0.578	0.531	0.66	0.657	0.678	0.578		
naphthalene	0	0		0.463	0.889	0.828	0.911	1.026	1.005	0.951		
TOTAL BTEXTMB	0.043	1.533	2.12	60.311	89.885	63.874	60.984	56.912	56.728	50.185		
Dissolved Oxygen				0.37	0.64	0.62	0.5	0.57	0.54			
Compound	Sample ID: E-21	E-104	E-215	E-284	E-329	E-405	E-444	E-477	E-510	E-549		
	Date: 22-Nov-85	25-Apr-86	30-May-86	12-Jun-86	24-Jun-86	9-Jul-86	23-Jul-86	6-Aug-86	21-Aug-86	4-Sep-86		
Benzene	0.037	0.018	9.308	2.392	1.282	2.398	1.027	2.480	0.453	0.416		
Toluene	0.024	0.049	28.183	35.074	38.960	18.724	21.153	18.526	15.21	9.158		
Ethylbenzene	0.000	0.000	3.854	5.519	6.224	7.601	7.953	6.908	6.908	8.857		
p,m-xylene	0.000	0.000	8.176	11.784	17.304	16.129	17.124	16.588	15.656	13.366		
o-xylene	0.000	0.000	3.461	5.083	7.482	7.015	7.049	6.519	5.88	4.998		
1,3-trimethylbenzene	0.000	0.000	0.318	0.444	0.592	0.662	0.649	0.66	0.66	0.608		
1,2,4-trimethylbenzene	0.000	0.000	1.026	1.482	2.192	2.037	2.196	2.238	2.372	2.16		
1,2,3-trimethylbenzene	0.000	0.000	0.280	0.411	0.607	0.553	0.664	0.684	0.695	0.632		
naphthalene	0.000	0.000	0.000	0.547	0.842	0.837	0.974	1.025	0.835	0.981		
TOTAL BTEXTMB	0.061	0.067	55.614	62.716	77.685	55.884	59.902	56.227	48.787	42.178		
Dissolved Oxygen			0.94	0.57	0.82	1.22	1	0.47	0.25			

US EPA DENITRIFICATION STUDY												
CONTROL CELL												
ALL PORTS AT LEVEL -6 (100 CM DEPTH)												
Compound	Sample ID:	E-29	E-113	E-217	E-286	E-331	E-407	E-447	E-480	E-513	E-552	
	Date:	22-Nov-95	25-Apr-96	30-May-96	12-Jun-96	24-Jun-96	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	
Benzene					19.703	33.844	30.531	31.173	28.575	17.779	15.057	
Toluene			0.104	17.64	30.877	54.377	48.066	52.248	52.313	48.111	46.135	
Ethylbenzene			0.054	27.573	3.993	6.777	6.173	6.657	6.576	6.522	5.825	
p,m-xylene			0	7.393	8.397	14.116	12.898	13.921	13.779	13.814	12.281	
o-xylene			0.036	3.138	3.539	6.040	5.627	6.056	5.949	5.908	5.302	
1,3,5-trimethylbenzene			0	0.287	0.325	0.559	0.489	0.542	0.525	0.515	0.457	
1,2,4-trimethylbenzene			0	0.941	1.063	1.772	1.645	1.756	1.731	1.768	1.595	
1,2,3-trimethylbenzene			0	0.264	0.289	0.496	0.451	0.531	0.529	0.517	0.459	
naphthalene			0	0.329	0.376	0.786	0.677	0.734	0.799	0.866	0.729	
TOTAL BTEXTMB			0.014	61.107	68.572	118.759	106.555	113.616	110.776	96.638	87.84	
Dissolved Oxygen			0.194	1.18	0.46	0.69	0.94	0.97	0.77	0.49		
LOCATION PZ3E-6												
Compound	Sample ID:	E-37	E-122	E-219	E-286	E-333	E-382	E-450	E-483	E-519	E-555	
	Date:	22-Nov-95	25-Apr-96	30-May-96	12-Jun-96	24-Jun-96	3-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96	4-Sep-96	
	Elapsed Time (days)	-174	-19	18	29	41	50	70	84	99	113	
Benzene					7.983	4.287	1.184	1.195	0.421	0.613	0.450	
Toluene		0.039	4.689	15.271	31.224	55.515	47.879	45.729	38.985	16.935	11.017	
Ethylbenzene		0.248	17.674	28.163	3.804	6.862	6.579	6.656	7.417	7.806	7.211	
p,m-xylene		0.54	3.524	3.614	8.136	14.420	13.725	13.958	15.675	16.607	15.310	
o-xylene		1.248	7.413	7.68	6.310	6.182	6.235	6.913	7.087	7.138	6.556	
1,3,5-trimethylbenzene		0.434	3	3.274	3.525	6.310	6.182	6.235	6.913	7.087	6.556	
1,2,4-trimethylbenzene		0.09	0.311	0.321	0.319	0.581	0.533	0.522	0.598	0.603	0.532	
1,2,3-trimethylbenzene		0.26	1.08	1.028	1.024	1.655	1.655	1.801	1.939	2.117	1.872	
naphthalene		0.067	0.284	0.284	0.288	0.511	0.493	0.485	0.583	0.620	0.544	
TOTAL BTEXTMB		0.037	0.305	0.358	0.362	0.764	0.744	0.741	0.814	0.855	0.922	
Dissolved Oxygen		2.959	38.26	60.893	56.667	91.105	79.154	77.322	63.009	53.294	44.414	
total fe					0.81	1.05	3.2	2.09	1.2	0.75	0.5	
sulfide					0.06	0.1	0.1	2.99		0.05	7.36	
					10.6							

US EPA DENITRIFICATION STUDY												
CONTROL CELL												
INJECTION AND EXTRACTION PORTS												
Aromatic hydrocarbon detection limits												
All concentrations in mg/L												
LOCATION: INJECTION PORT												
Compound	E-176	E-160	E-194	E-276	E-320	E-365	E-398	E-431	E-467	E-500	E-538	
	15-May-96	17-May-96	21-May-96	4-Jun-96	12-Jun-96	24-Jun-96	3-Jul-96	9-Jul-96	23-Jul-96	6-Aug-96	21-Aug-96	
pw3-2												
15-Apr-96	1	3	7	21	29	41	50	56	70	84	99	
Benzene	4.034	5.852	7.595	10.387	12.962	12.834	10.883	10.475	8.125	6.729	4.026	
Toluene	13.062	10.186	13.373	17.055	23.412	21.561	35.822	34.981	34.001	33.796	34.39	
Ethylbenzene	2.407	1.301	1.691	2.024	2.741	4.446	4.838	5.082	5.505	5.630	6.672	
p,m-xylene	5.102	2.672	3.444	4.218	5.709	9.256	10.234	10.612	11.520	11.873	14.304	
o-xylene	2.007	1.121	1.449	1.725	2.445	4.044	4.545	4.700	5.047	5.135	6.033	
1,3,5-trimethylbenzene	0.256	0.13	0.169	0.175	0.206	0.31	0.334	0.344	0.407	0.409	0.518	
1,2,4-trimethylbenzene	0.742	0.308	0.414	0.458	0.643	1.064	1.18	1.197	1.321	1.431	1.773	
1,2,3-trimethylbenzene	0.206	0.089	0.116	0.139	0.182	0.18	0.284	0.319	0.335	0.411	0.523	
naphthalene	0.23	0.127	0.234	0.165	0.214	0.221	0.434	0.456	0.473	0.522	0.714	
TOTAL BTEX/TMB	28.046	21.816	28.485	36.356	48.514	67.803	68.711	68.199	66.859	66.082	68.953	
NITRATE	<0.05	3.17	<0.05	<0.05								
NITRITE	<0.05	<0.05	<0.05	<0.05								
TOTAL FE				0.68								0.63
SULFATE				4.66								5.53

US EPA DENITRIFICATION STUDY									
CONTROL CELL									
INJECTION AND EXTRACTION PORTS									
Aromatic hydrocarbon detection limits									
All concentrations in mg/L									
LOCATION: INJECTION PORT									
Compound									
Benzene									
Toluene									
Ethylbenzene									
p,m-xylene									
o-xylene									
1,3,5-trimethylbenzene									
1,2,4-trimethylbenzene									
1,2,3-trimethylbenzene									
naphthalene									
NITRATE									
NITRITE									
TOTAL FE									
SULFATE									
LOCATION: EXTRACTION PORT									
Compound	E-572	E-608	E-624	E-676	E-682	E-712	E-758	E-765	E-770
	4-Sep-96	25-Sep-96	2-Oct-96	16-Oct-96	28-Oct-96	4-Nov-96	2-May-97	9-May-97	26-May-97
	113	134	141	155		174	175	182	199
Benzene	3.074	1.818	1.301	0.584		0.559	0.53	0.413	0.306
Toluene	31.002	30.409	24.026	16.217		19.469	21.447	19.538	18.072
Ethylbenzene	6.004	6.686	5.417	3.799		4.968	5.23	5.026	4.87
p,m-xylene	12.81	14.379	11.687	8.266		10.684	11.225	10.738	10.524
o-xylene	5.433	5.988	4.846	3.389		4.391	4.599	4.228	4.055
1,3,5-trimethylbenzene	0.44	0.523	0.425	0.318		0.445	0.446	0.417	0.451
1,2,4-trimethylbenzene	1.563	1.858	1.504	1.111		1.506	1.572	1.506	1.616
1,2,3-trimethylbenzene	0.457	0.543	0.441	0.322		0.402	0.434	0.415	0.437
naphthalene	0.668	0.732	0.554	0.441		0.546	0.562	0.319	0.335
TOTAL BTEXTMB	61.451	62.934	50.201	34.447		42.97	46.045	42.6	40.666
NITRATE									
NITRITE									
TOTAL FE			0.5		0.72				0.79
SULFATE			7.67		4.04				6.62

U.S. EPA - Denitrification Study							
Vertical Profile Data							
Control Cell							
All concentrations in mg/L.							
LOCATION: PZ3E							
date	date	Elapsed Time (days)	sample	Port	depth (cm)	benzene	toluene
25-Apr-96	35180	-19	E-117	PZ3E-1	30	307.841	636.971
25-Apr-96	35180	-19	E-118	PZ3E-2	60	36.932	64.831
25-Apr-96	35180	-19	E-119	PZ3E-3	90	40.563	69.007
25-Apr-96	35180	-19	E-120	PZ3E-4	120	31.292	48.774
25-Apr-96	35180	-19	E-121	PZ3E-5	150	43.094	82.363
25-Apr-96	35180	-19	E-122	PZ3E-6	180	4.689	17.674
25-Apr-96	35180	-19	E-123	PZ3E-7	210	2.412	5.693
25-Apr-96	35180	-19	E-124	PZ3E-8	240	3.259	7.714
25-Apr-96	35180	-19	E-125	PZ3E-9	270	2.614	5.725
4-Jun-96	35220	21	E-263	PZ3E-2	60	0.485	4.301
4-Jun-96	35220	21	E-262	PZ3E-3	90	18.264	37.194
4-Jun-96	35220	21	E-261	PZ3E-4	120	21.313	32.421
4-Jun-96	35220	21	E-260	PZ3E-5	150	38.049	62.504
4-Jun-96	35220	21	E-259	PZ3E-6	180	2.652	11.898
4-Jun-96	35220	21	E-258	PZ3E-7	210	14.869	32.294
3-Jul-96	35249	50	E-386	PZ3E-2	60	0.160	0.803
3-Jul-96	35249	50	E-385	PZ3E-3	90	1.346	53.582
3-Jul-96	35249	50	E-384	PZ3E-4	120	19.782	46.745
3-Jul-96	35249	50	E-383	PZ3E-5	150	29.661	53.748
3-Jul-96	35249	50	E-382	PZ3E-6	180	1.164	47.879
3-Jul-96	35249	50	E-381	PZ3E-7	210	5.465	34.935
21-Aug-96	35298	99	E-515	PZ3E-2	60	0.222	0.892
21-Aug-96	35298	99	E-516	PZ3E-3	90	0.376	28.767
21-Aug-96	35298	99	E-517	PZ3E-4	120	0.415	53.537
21-Aug-96	35298	99	E-518	PZ3E-5	150	13.174	51.563
21-Aug-96	35298	99	E-519	PZ3E-6	180	0.613	16.935
21-Aug-96	35298	99	E-520	PZ3E-7	210	5.338	22.484
2-Oct-96	35340	141	E-611	PZ3E-2	60	0.104	0.354
2-Oct-96	35340	141	E-612	PZ3E-3	90	0.31	5.753
2-Oct-96	35340	141	E-613	PZ3E-4	120	0.301	51.576
2-Oct-96	35340	141	E-614	PZ3E-5	150	0.497	49.433
2-Oct-96	35340	141	E-615	PZ3E-6	180	0.301	5.895
2-Oct-96	35340	141	E-616	PZ3E-7	210	0.643	16.286
18-Jul-97	35629	430	E-813	PZ3E-1	30	0.238	5.416
18-Jul-97	35629	430	E-806	PZ3E-2	60	0.138	2.942
18-Jul-97	35629	430	E-807	PZ3E-3	90	0.285	1.241
18-Jul-97	35629	430	E-808	PZ3E-4	120	0.217	43.229
18-Jul-97	35629	430	E-809	PZ3E-5	150	0.299	47.032
18-Jul-97	35629	430	E-810	PZ3E-6	180	0.218	2.029
18-Jul-97	35629	430	E-811	PZ3E-7	210	0.138	4.127

U.S. EPA - Denitrification Station							
Vertical Profile Data							
Control Cell							
All concentrations in mg/L.							
LOCATION: PZ3E							
date	ethylbenzene	p,m-xylene	o-xylene	1,3,5-TMB	1,2,4-TMB	1,2,3-TMB	naphthalene
25-Apr-96	274.2	657.444	213.719	86.785	242.648	61.049	31.648
25-Apr-96	13.162	29.178	11.402	3.242	8.981	2.174	2.261
25-Apr-96	21.048	41.545	14.064	5.605	13.357	3.33	3.306
25-Apr-96	6.247	13.145	5.476	0.57	1.864	0.507	1.026
25-Apr-96	23.212	45.865	15.691	5.872	14.041	3.482	3.095
25-Apr-96	3.524	7.413	3	0.311	1.06	0.284	0.305
25-Apr-96	0.833	1.67	0.722	0.073	0.198	0.062	0.054
25-Apr-96	0.879	1.76	0.782	0.058	0.219	0.049	0
25-Apr-96	0.614	1.236	0.555	0.103	0.268	0.032	0
4-Jun-96	0.891	2.04	0.836	0.194	0.55	0.145	0.157
4-Jun-96	6.265	13.128	5.323	1.017	2.795	0.717	0.595
4-Jun-96	4.31	9.051	3.777	0.394	1.278	0.35	0.445
4-Jun-96	16.276	33.333	12.518	3.588	9.651	2.357	1.88
4-Jun-96	2.232	4.91	2.004	0.284	0.874	0.232	0.258
4-Jun-96	3.965	8.427	3.645	0.331	1.102	0.306	0.402
3-Jul-96	0.338	0.831	0.299	0.097	0.321	0.031	0.058
3-Jul-96	7.498	15.621	6.740	0.872	2.669	0.769	1.006
3-Jul-96	5.975	12.417	5.500	0.492	1.737	0.459	0.794
3-Jul-96	12.821	25.806	9.965	3.106	7.948	1.845	1.689
3-Jul-96	6.579	13.725	6.182	0.533	1.855	0.493	0.744
3-Jul-96	4.008	8.135	3.671	0.196	0.676	0.195	0.208
21-Aug-96	0.774	1.912	0.627	0.189	0.529	0.153	0.103
21-Aug-96	7.578	16.135	6.978	0.65	2.26	0.636	0.893
21-Aug-96	7.04	14.945	6.378	0.556	1.987	0.577	0.798
21-Aug-96	7.162	15.314	6.472	0.646	2.186	0.63	0.863
21-Aug-96	7.806	16.607	7.138	0.603	2.117	0.62	0.855
21-Aug-96	6.748	14.502	6.054	0.438	1.566	0.474	0.58
2-Oct-96	0.435	1.101	0.376	0.114	0.329	0.087	0.056
2-Oct-96	7.972	16.805	7.338	0.646	2.237	0.637	0.844
2-Oct-96	6.427	13.576	5.821	0.516	1.799	0.513	0.665
2-Oct-96	6.393	13.5	5.782	0.522	1.811	0.516	0.674
2-Oct-96	7.809	16.921	6.795	0.614	2.16	0.625	0.897
2-Oct-96	6.275	13.832	5.467	0.457	1.655	0.489	0.586
18-Jul-97	2.121	12.366	6.108	1.239	3.565	1.069	0.142
18-Jul-97	1.321	3.239	1.227	0.194	0.69	0.168	0.128
18-Jul-97	8.76	18.409	7.581	0.653	2.343	0.645	0.97
18-Jul-97	6.028	12.536	5.308	0.422	1.661	0.405	0.668
18-Jul-97	5.984	12.456	5.225	0.426	1.667	0.404	0.644
18-Jul-97	5.608	12.506	4.379	0.547	1.99	0.554	0.782
18-Jul-97	3.775	8.534	3.08	0.32	1.279	0.317	0.291

U.S. EPA Denitrification Study													
Control Cell													
Core extract samples													
Zeros used for not-detected samples													
Method detection limits provided in text.													
			bulk density	2.15	g/cm ³								
Core 3B			depth interval:	0.14	m								
Depth (cm TOC)	Sample ID		Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	depth int. midpoint
0.07	49		0.0	6.2	4.7	16.2	5.8	5.3	11.1	2.5	0.0	51.8	7
0.21	50		0.0	0.0	0.0	0.0	0.0	0.0	4.1	0.0	0.0	4.1	21
0.35	51		0.0	0.0	2.9	16.9	5.0	7.5	17.5	4.1	0.0	54.0	35
0.49	52		15.6	144.8	156.6	386.2	106.1	88.6	240.7	55.0	50.5	1244.1	49
0.63	53		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	63
0.77	54		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	77
0.91	55		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	91
1.05	56		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	105
		g/m ²	4.7	45.4	49.4	126.2	35.2	30.5	62.3	18.6	15.2	407.5	
Core 3C			depth interval:	0.15									
Depth (cm TOC)	Sample ID		Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
0.08	41		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.5
0.23	42		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	22.5
0.38	43		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	37.5
0.53	44		11.2	24.1	72.1	179.6	49.0	75.2	199.5	42.6	32.3	685.7	52.5
0.68	45		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	67.5
0.83	46		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	82.5
0.98	47		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	97.5
1.13	48		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	112.5
		g/m ²	3.6	7.8	23.2	57.9	15.8	24.3	64.3	13.7	10.4	221.1	
Core 3D			depth interval:	0.144									
Depth (cm TOC)	Sample ID		Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
0.07	57		0.0	0.0	0.0	5.9	0.0	0.0	5.2	0.0	0.0	11.2	7.2
0.22	58		0.0	0.0	0.0	5.5	0.0	0.0	5.5	0.0	0.0	11.1	21.6
0.50	60		7.8	50.3	20.5	50.3	15.1	38.6	74.2	16.3	12.3	285.4	50.4
0.65	61		0.0	0.0	0.0	4.5	0.0	0.0	0.0	0.0	0.0	4.5	64.8
0.79	62		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	79.2
0.94	63		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	93.6
1.08	64		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	108
		g/m ²	2.4	15.6	6.4	20.5	4.7	11.9	26.3	5.1	3.8	96.6	

U.S. EPA Denitrification Study												
Control Cell												
Core extract samples												
Zeros used for not-detected samples												
Method detection limits provided in text.												
Core 3E												
depth interval: 0.15												
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
	0.075	0.0	3.7	3.1	8.8	2.7	3.3	8.4	0.0	0.0	30.0	7.5
	0.2	0.0	3.3	3.2	8.0	0.0	3.1	7.4	0.0	0.0	25.0	22.5
	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	37.5
	0.5	0.0	15.0	0.0	0.0	0.0	0.0	3.6	0.0	0.0	18.5	52.5
	0.7	5.3	18.6	8.2	21.1	4.3	30.8	77.8	13.9	3.9	184.0	67.5
	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	82.5
	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	97.5
	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	112.5
		1.7	13.1	4.7	12.2	2.3	12.0	31.3	4.5	1.3	83.1	
Core 3F												
depth interval: 0.143												
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
	0.0715	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.125
	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21.4
	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	35.6
	0.5	0.0	24.8	12.8	31.2	10.9	15.0	32.6	7.5	7.7	142.5	48.9
	0.6	10.4	37.7	26.9	69.5	16.8	51.1	137.8	26.9	10.3	387.5	64.1
	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	78.4
	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	92.6
	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	106.9
		3.2	19.2	12.2	31.0	8.5	20.3	52.4	10.8	5.5	162.9	
Core 3G												
depth interval: 0.152												
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.6
	0.2	0.0	12.9	18.1	45.5	14.4	14.6	38.5	8.4	7.0	159.4	22.8
	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	38
	0.5	37.3	247.8	183.9	475.2	144.2	202.4	487.6	104.0	71.5	1973.8	53.2
	0.7	33.2	134.8	463.1	1078.6	331.5	157.2	424.3	96.5	95.7	2614.9	68.4
	0.8	14.1	101.2	200.1	434.7	160.2	63.2	170.8	38.3	36.5	1218.9	83.6
	1.0	17.0	323.4	224.6	492.2	179.4	73.0	186.0	44.4	43.3	1593.5	98.8
	1.1	0.0	3.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.7
		33.2	269.2	359.4	825.5	271.1	166.8	433.7	95.3	83.0	2537.3	114

U.S. EPA Denitrification Study												
Control Cell												
Core extract samples												
Zeros used for not-detected samples												
Method detection limits provided in text.												
Core 3H		0.154										
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
	0.077	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.7
	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	23.1
	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	38.5
	0.5	9.9	86.6	52.0	122.7	37.2	66.3	168.8	34.6	20.6	600.7	53.9
	0.7	10.7	46.1	198.1	431.0	145.1	73.0	181.5	40.6	44.1	1162.2	69.3
	0.8	32.9	755.6	536.0	1178.6	433.7	177.9	491.0	112.7	116.3	3834.6	84.7
	1.0	14.2	512.8	229.5	506.1	187.0	79.9	220.0	49.3	56.5	1855.3	100.1
	1.2	0.0	6.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.3	115.5
		22.4	487.3	332.9	741.2	265.9	131.5	351.4	78.5	78.6	2469.8	
Core 3I		0.14										
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7
	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21
	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	35
	0.5	19.0	198.1	164.0	388.8	119.9	111.9	295.2	64.9	54.8	1376.6	49
	0.8	26.7	194.8	364.3	806.5	266.4	112.5	308.1	70.0	67.3	2296.6	63
	0.8	20.2	422.8	326.8	718.7	266.1	106.9	295.6	67.8	66.7	2291.6	77
	0.9	12.9	478.2	194.0	427.5	157.9	65.8	182.2	41.0	46.8	1606.3	91
	1.1	21.9	766.7	347.7	765.5	279.5	119.4	325.1	74.0	83.4	2783.2	105
		30.3	608.2	420.5	835.2	334.0	155.5	423.3	95.6	96.0	3098.6	

U.S. EPA Denitrification Study												
Control Cell												
Core extract samples												
Zeros used for not-detected samples												
Method detection limits provided in text.												
Core 3J												
depth interval: 0.145												
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
0.07	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7.25
0.22	2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	21.75
0.36	3	0.0	36.1	22.1	134.2	53.7	44.0	98.7	23.3	9.6	421.8	36.25
0.51	4	21.4	131.9	39.1	99.3	30.9	142.2	304.7	61.6	36.6	867.8	50.75
0.65	5	21.7	77.4	244.6	600.9	162.4	107.4	291.4	66.5	66.3	1638.6	65.25
0.80	6	16.6	68.4	230.1	503.7	184.3	71.4	183.2	43.8	41.6	1353.2	79.75
0.94	7	5.9	131.3	84.7	185.4	67.3	27.3	73.5	16.3	18.2	607.8	94.25
1.09	8	42.3	1605.0	632.1	1371.2	494.8	208.5	557.4	126.0	123.1	5160.5	108.75
1.74	9	11.7	228.4	183.6	404.1	145.4	59.3	158.6	34.9	38.8	1264.9	159.25
1.86	10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	173.75
2.03	11	0.0	0.0	0.0	6.8	17.4	3.0	8.6	0.0	0.0	40.3	188.25
	12	0.0	0.0	0.0	0.0	4.8	0.0	0.0	0.0	0.0	4.8	202.75
		57.6	1400.1	758.6	1703.3	597.3	307.5	795.1	176.6	164.5	5958.9	
Core 3K												
depth interval: 0.14												
Depth (cm TOC)	Sample ID	Ben (mg/kg)	Tol (mg/kg)	Eben (mg/kg)	p,m-Xyl (mg/kg)	o-Xyl (mg/kg)	135-TMB (mg/kg)	124-TMB (mg/kg)	123-TMB (mg/kg)	naph (mg/kg)	Total (mg/kg)	
0.1	89	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	7
0.2	96	0.0	0.0	0.0	6.2	3.1	4.1	6.4	0.0	0.0	19.8	21
0.4	90	17.8	332.5	206.7	490.7	176.4	98.3	252.0	57.0	43.7	1675.1	35
0.5	91	6.1	58.1	20.9	49.0	18.4	20.8	33.9	8.6	11.6	227.5	49
0.6	92	17.8	67.8	192.1	497.9	109.1	87.4	237.9	55.1	59.5	1324.6	63
0.8	83	14.6	49.2	197.5	432.9	160.6	59.8	163.3	36.1	34.8	1148.7	77
0.9	94	21.8	330.9	330.2	722.2	265.1	105.7	283.3	64.1	61.7	2185.2	91
1.1	95	36.1	1337.0	526.3	1151.8	413.6	172.0	462.5	104.7	101.7	4305.7	105

299

U.S. EPA Water con Gasoline s	19-Oct-95	31-Oct-95	29-Feb-96	Depth (m)	C3U2 Depth (cm)	16-Oct-95 (%)	16-Oct-95 (Saturation	17-Oct-95 (%)	19-Oct-95 (%)	31-Oct-95 (%)	29-Feb-96 (%)	Depth (m)
	(%)	(%)	(%)									
	16.01	15.75	0	1.967	194.7	0	0.00	17.1	18.44	16.53	17.12	1.947
	44.27	44.05	45.48	1.867	184.7	46.49	100.85	48.01	45.45	46.09	48.68	1.847
	43.68	43.39	42.92	1.767	174.7	47.09	102.15	42.03	47.23	43.91	45.39	1.747
	43.93	44.43	45.46	1.667	164.7	44.91	97.42	46.73	44.14	47.9	45.23	1.647
	41.27	41.59	41.72	1.567	154.7	45.59	98.89	45.77	44.71	45.39	47.18	1.547
	35.11	38.69	40.02	1.467	144.7	44	95.44	43.56	44.82	45.54	45.24	1.447
	34.38	37.45	40.55	1.367	134.7	46.1	100.00	46.71	45.73	46.97	46.96	1.347
	29.38	37.75	38.92	1.267	124.7	38.69	83.93	40.19	42.44	42.88	45.07	1.247
	29.3	39.25	40.48	1.167	114.7	36.21	78.55	37.69	41.62	45.05	45.93	1.147
	26.35	35.86	39.2	1.067	104.7	21.99	47.70	25.82	33.86	41.32	42.37	1.047
	25.98	34.92	38.69	0.967	94.7	19.49	42.28	23.06	34.09	39.08	42.96	0.947
	23.82	36.71	39.85	0.867	84.7	19.64	42.60	21.22	25.5	40.2	44.84	0.847
	21.42	36.9	38.1	0.767	74.7	17.79	38.59	17.89	18.99	38.75	39.84	0.747
	15.71	27.28	35.15	0.667	64.7	14.89	32.30	14.83	16.44	29.38	41.46	0.647
	11.97	11.93	41.63	0.567	54.7	15.46	33.54	14.88	15.16	13.54	42.39	0.547
	27.01	26.4	39.75	0.467	44.7	25.99	56.38	24.85	23.55	25	42.02	0.447
	20.19	20.76	39.43	0.367	34.7	18.55	40.24	17.6	17.35	17.58	45.07	0.347
	15.75	16.81	35.34	0.267	24.7	17.1	37.09	18.44	16.53	17.12	38.8	0.247

U.S. EPA Denitrification Study							
Tracer Test Data, Injection and Extraction Concentrations							
Bromide determinations June 1997 using electrode							
Injection Ports							
Location	Time	Elapsed Time (hr:min)	Br (mg/L)	Sample ID	Time (hr)	Br (mg/L)	C/Co
	1/1/00 11:40						
Control Cell	1/1/00 12:40	1:00:00	262.55	T-1	1.00	262.55	1.009
	1/1/00 15:00	3:20:00	238.15	T-13 n=2	3.33	238.15	0.915
	1/1/00 22:50	11:10:00	272.9	T-25 n=2	11.17	272.9	1.049
	1/2/00 5:40	18:00:00	278	T-37 n=2	18	278	1.069
	1/2/00 11:00	23:20:00	262.55	T-49 n=2	23.33	262.55	1.009
	1/2/00 16:00	28:20:00	257.35	T-71 n=2	28.33	257.35	0.989
	1/2/00 23:10	35:30:00	258.75	T-83 n=2	35.5	258.75	0.995
	1/3/00 6:15	42:35:00	250.9	T-85 n=2	42.58	250.9	0.984
	1/3/00 11:15	47:35:00	0.9	T-107	47.58	0.9	0.003
		mean	260.14				
		S.D.	12.38				
Location	Time	Elapsed Time	Br (mg/L)	Sample ID	Time	Br (mg/L)	C/Co
	1/1/00 11:40						
Nitrate Cell	1/1/00 12:40	1:00:00	262.55	T-2	1.00	262.55	1.010
	1/1/00 15:00	3:20:00	242.85	T-14 n=2	3.33	242.85	0.934
	1/1/00 22:50	11:10:00	268	T-28 n=2	11.17	268	1.031
	1/2/00 5:40	18:00:00	267.45	T-38 n=2	18	267.45	1.028
	1/2/00 11:00	23:20:00	262.55	T-50 n=2	23.33	262.55	1.010
	1/2/00 16:00	28:20:00	267.45	T-72 n=2	28.33	267.45	1.028
	1/2/00 23:10	35:30:00	258.75	T-84 n=2	35.5	258.75	0.995
	1/3/00 6:15	42:35:00	250.9	T-86 n=2	42.58	250.9	0.985
	1/3/00 11:15	47:35:00	0.6	T-108	47.58	0.6	0.002
		mean	260.06				
		S.D.	9.00				
Extraction Ports							
Location	Time	Elapsed Time	Br (mg/L)	Sample ID	Time	Br (mg/L)	C/Co
	1/1/00 11:40						
Control Cell	1/4/00 10:40	71:00:00	1.3	T-158	71.00	1.3	0.005
	1/5/00 13:00	97:20:00	44.1	T-208	97.33	44.1	0.170
	1/5/00 20:40	105:00:00	51.5	T-227	105.00	51.5	0.198
	1/6/00 7:05	115:25:00	62.2	T-238	115.42	62.2	0.239
	1/6/00 14:25	122:45:00	67.1	T-279	122.75	67.1	0.256
	1/6/00 20:20	128:40:00	81.4	T-293	128.67	81.4	0.313
	1/7/00 6:45	139:05:00	67.1	T-314	139.08	67.1	0.258
	1/7/00 14:50	147:10:00	64.5	T-345	147.17	64.5	0.248
	1/8/00 7:30	163:50:00	55.1	T-363	163.83	55.1	0.212
	1/8/00 14:00	170:20:00	50.9	T-375	170.33	50.9	0.196
	1/8/00 21:05	177:25:00	47.1	T-387	177.42	47.1	0.181
	1/9/00 13:50	194:10:00	31.7	T-422	194.08	31.7	0.122
	1/10/00 9:00	213:20:00	30.5	T-424	213.33	30.5	0.117
	1/11/00 9:00	237:20:00	21.6	T-447	237.33	21.6	0.083
	1/12/00 8:45	261:05:00	17.8	T-469	261.08	17.8	0.068
	1/13/00 10:55	287:15:00	15.3	T-488	287.25	15.3	0.059
	1/15/00 9:30	333:50:00	13.6	T-497	333.83	13.6	0.052
	1/17/00 13:30	385:50:00	10.1	T-508	385.83	10.1	0.039

U.S. EPA Denitrification Study							
Tracer Test Data, Injection and Extraction Concentrations							
Bromide determinations June 1997 using electrode							
		Elapsed	Br			Br	
Location	Time	Time	(mg/L)	Sample ID	Time	(mg/L)	C/Co
	1/1/00 11:40						
Nitrate Cell	1/4/00 10:45	71:05:00	0.7	T-157	71.08	0.7	0.003
	1/5/00 13:00	97:20:00	12.3	T-207	97.33	12.3	0.047
	1/5/00 20:40	105:00:00	24.7	T-228	105.00	24.7	0.095
	1/6/00 7:05	115:25:00	44	T-239	115.42	44	0.169
	1/6/00 14:25	122:45:00	49.4	T-280	122.75	49.4	0.190
	1/6/00 20:20	128:40:00	57.6	T-294	128.67	57.6	0.221
	1/7/00 6:45	139:05:00	91.3	T-315	139.06	91.3	0.351
	1/7/00 14:50	147:10:00	103.6	T-346	147.17	103.6	0.398
	1/8/00 7:30	163:50:00	92	T-364	163.83	92	0.354
	1/8/00 14:00	170:20:00	72.6	T-376	170.33	72.6	0.279
	1/8/00 21:05	177:25:00	62	T-388	177.42	62	0.238
	1/9/00 13:50	194:10:00	38.6	T-423	194.08	38.6	0.148
	1/10/00 9:00	213:20:00	37.1	T-425	213.33	37.1	0.143
	1/11/00 9:00	237:20:00	23.3	T-448	237.33	23.3	0.090
	1/12/00 8:45	261:05:00	20	T-470	261.08	20	0.077
	1/13/00 10:55	287:15:00	15.3	T-489	287.25	15.3	0.059
	1/15/00 9:30	333:50:00	11.7	T-498	333.83	11.7	0.045
	1/17/00 13:30	385:50:00	5.9	T-509	385.83	5.9	0.023

U.S. EPA Denitrification Study							
Tracer Test Data, Control Cell, Level 2 (60 cm depth)							
Bromide determinations June 1997 using electrode							
		Elapsed	Br			Br	
Location	Time	Time	(mg/L)	Sample ID	Time	(mg/L)	C/Co
PZ3C	1/1/00 12:45	1:05:00	5.9	T-5	1:08	5.9	0.023
	1/1/00 15:25	3:45:00	211.1	T-17	3:75	211.1	0.811
	1/1/00 22:50	11:10:00	86.1	T-29	11:16	86.1	0.331
	1/2/00 5:43	18:03:00	4.3	T-41	18:05	4.3	0.017
	1/2/00 11:03	23:23:00	246.7	T-53	23:38	246.7	0.948
	1/2/00 16:00	28:20:00	246.7	T-63	28:33	246.7	0.948
	1/2/00 23:10	35:30:00	246.7	T-75	35:50	246.7	0.948
	1/3/00 6:20	42:40:00	260.8	T-89	42:67	260.8	1.003
	1/3/00 11:00	47:20:00	250.9	T-99	47:33	250.9	0.964
	1/3/00 15:50	52:10:00	4.3	T-114	49:16	4.3	0.017
	1/3/00 20:55	57:15:00	1.3	T-124	57:25	1.3	0.005
	1/4/00 11:10	71:30:00	223.5	T-160	71:50	223.5	0.859
		Elapsed	Br			Br	
Location	Time	Time	(mg/L)	Sample ID	Time	(mg/L)	C/Co
PZ3D	1/1/00 12:48	1:08:00	6.1	T-6	1:13	6.1	0.023
	1/1/00 15:25	3:45:00	237.3	T-18	3:75	237.3	0.912
	1/1/00 22:50	11:10:00	263.3	T-30	11:16	263.3	1.012
	1/2/00 5:44	18:04:00	246.7	T-42	18:07	246.7	0.948
	1/2/00 11:03	23:23:00	237.3	T-54	23:38	237.3	0.912
	1/2/00 16:00	28:20:00	246.7	T-64	28:33	246.7	0.948
	1/2/00 23:10	35:30:00	250.9	T-76	35:50	250.9	0.964
	1/3/00 6:20	42:40:00	250.9	T-90	42:67	250.9	0.964
	1/3/00 11:00	47:20:00	8.7	T-100	47:33	8.7	0.033
	1/3/00 15:55	52:15:00	1.3	T-115	49:25	1.3	0.005
	1/3/00 20:55	57:15:00	1.8	T-125	57:25	1.8	0.007
	1/4/00 11:10	71:30:00	1.3	T-161	71:50	1.3	0.005
		Elapsed	Br			Br	
Location	Time	Time	(mg/L)	Sample ID	Time	(mg/L)	C/Co
PZ3E	1/1/00 12:49	1:09:00	256.5	T-7	1:15	256.5	0.986
	1/1/00 15:25	3:45:00	237.3	T-19	3:75	237.3	0.912
	1/1/00 22:50	11:10:00	256.5	T-31	11:17	256.5	0.986
	1/2/00 5:45	18:05:00	246.7	T-43	18:08	246.7	0.948
	1/2/00 11:04	23:24:00	246.7	T-55	23:38	246.7	0.948
	1/2/00 16:00	28:20:00	246.7	T-65	28:33	246.7	0.948
	1/2/00 23:10	35:30:00	250.9	T-77	35:50	250.9	0.964
	1/3/00 6:20	42:40:00	250.9	T-91	42:67	250.9	0.964
	1/3/00 11:05	47:25:00	42.5	T-101	47:42	42.5	0.163
	1/3/00 13:00	49:20:00	12.8	T-111	49:33	12.8	0.049
	1/3/00 15:55	52:15:00	12.3	T-116	52:25	12.3	0.047
	1/3/00 20:55	57:15:00	7.8	T-126	57:25	7.8	0.030
	1/4/00 11:10	71:30:00	3.6	T-162	71:50	3.6	0.014

U.S. EPA Denitrification Study
Tracer Test Data, Control Cell, Level 4 (120 cm depth)
Bromide determinations June 1997 using electrode

Co = 260.14 mg/L

Location	Time	Elapsed Time (hr:min)	Br	Sample ID	Time (hr)	Br	C/Co
			(mg/L)			(mg/L)	
		35:40:00					
PZ3A	1/3/00 21:05	57:25:00	8.7	T-132	57.4	8.7	0.033
	1/4/00 6:10	66:30:00	164.1	T-141	66.5	164.1	0.631
	1/4/00 9:15	69:35:00	223.5	T-150	69.6	223.5	0.859
	1/4/00 11:20	71:40:00	232.2	T-168	71.7	232.2	0.893
	1/4/00 16:10	76:30:00	260.8	T-179	76.5	260.8	1.003
	1/4/00 21:15	81:35:00	271.1	T-188	81.6	271.1	1.042
	1/5/00 7:00	91:20:00	250.9	T-197	90.3	250.9	0.964
	1/5/00 13:00	97:20:00	308.6	T-208	97.3	308.6	1.186
	1/5/00 20:40	105:00:00	278.7	T-229	105.0	278.7	1.071
	1/6/00 7:05	115:25:00	124.3	T-240	115.4	124.3	0.478
	1/6/00 12:20	120:40:00	33.6	T-260	120.7	33.6	0.129
	1/6/00 20:25	128:45:00	7.5	T-295	128.8	7.5	0.029
	1/7/00 6:45	139:05:00	2.4	T-316	139.1	2.4	0.009

Location	Time	Elapsed Time (hr:min)	Br	Sample ID	Time (hr)	Br	C/Co
			(mg/L)			(mg/L)	
PZ3B	1/3/00 21:05	57:25:00	0.9	T-133	57.42	0.9	0.003
	1/4/00 6:10	66:30:00	45.9	T-142	66.50	45.9	0.176
	1/4/00 11:20	71:40:00	115.9	T-169	71.66	115.9	0.446
	1/4/00 16:10	76:30:00	191.5	T-180	76.50	191.5	0.736
	1/4/00 21:15	81:35:00	241.4	T-189	81.58	241.4	0.928
	1/5/00 7:01	91:21:00	232.3	T-198	91.35	232.3	0.893
	1/5/00 13:01	97:21:00	292.8	T-209	97.35	292.8	1.126
	1/5/00 20:40	105:00:00	289.6	T-230	105.00	289.6	1.113
	1/6/00 7:05	115:25:00	212.9	T-241	115.42	212.9	0.818
	1/6/00 12:20	120:40:00	129.1	T-261	120.66	129.1	0.496
	1/6/00 20:25	128:45:00	47.5	T-296	128.75	47.5	0.183
	1/7/00 6:45	139:05:00	13.3	T-317	139.08	13.3	0.051
	1/7/00 15:00	147:20:00	5	T-347	147.33	5	0.019

U.S. EPA Denitrification Study									
Tracer Test Data, Control Cell, Level 4 (120 cm depth)									
Bromide determinations June 1997 using electrode									
			Elapsed	Br				Br	
Location	Time	Time	(mg/L)	Sample ID	Time	(mg/L)	C/Co		
PZ3C	1/3/00 21:05	57:25:00	140.6	T-134	57.42	140.6	0.540		
	1/4/00 6:10	66:30:00	232.3	T-143	66.50	232.3	0.893		
	1/4/00 11:20	71:40:00	241.4	T-170	71.66	241.4	0.928		
	1/4/00 16:10	76:30:00	304.4	T-181	76.50	304.4	1.170		
	1/4/00 21:15	81:35:00	250.9	T-190	81.58	250.9	0.964		
	1/5/00 7:02	91:22:00	260.8	T-199	91.37	260.8	1.003		
	1/5/00 13:02	97:22:00	291.55	T-210	97.37	291.55	1.121	N=2	
	1/5/00 20:40	105:00:00	156.5	T-231	105.00	156.5	0.602		
	1/6/00 7:05	115:25:00	26.7	T-242	115.42	26.7	0.103		
	1/6/00 12:20	120:40:00	8.1	T-262	120.66	8.1	0.031		
	1/6/00 20:25	128:45:00	3.2	T-297	128.75	3.2	0.012		
	1/7/00 6:45	139:05:00	10.6	T-318	139.08	10.6	0.041		
				Elapsed	Br				Br
Location	Time	Time	(mg/L)	Sample ID	Time	(mg/L)	C/Co		
PZ3D	1/3/00 21:05	57:25:00	42.5	T-135	57.42	42.5	0.163		
	1/4/00 6:10	66:30:00	199	T-144	66.50	199	0.765		
	1/4/00 11:20	71:40:00	232.3	T-171	71.66	232.3	0.893		
	1/4/00 16:10	76:30:00	271.1	T-182	76.50	271.1	1.042		
	1/4/00 21:15	81:35:00	271.1	T-191	81.58	271.1	1.042		
	1/5/00 7:03	91:23:00	260.8	T-200	90.38	260.8	1.003		
	1/5/00 13:03	97:23:00	260.8	T-211	97.38	260.8	1.003		
	1/5/00 20:40	105:00:00	212.9	T-232	105.00	212.9	0.818		
	1/6/00 7:05	115:25:00	64.6	T-243	115.42	64.6	0.248		
	1/6/00 12:20	120:40:00	22	T-263	120.66	22	0.085		
	1/6/00 20:25	128:45:00	6.4	T-298	128.75	6.4	0.025		
	1/7/00 6:45	139:05:00	4.9	T-319	139.08	4.9	0.019		
				Elapsed	Br				Br
Location	Time	Time	(mg/L)	Sample ID	Time	(mg/L)	C/Co		
PZ3E	1/3/00 21:05	57:25:00	1	T-136	57.42	1	0.004		
	1/4/00 6:10	66:30:00	10.2	T-145	66.50	10.2	0.039		
	1/4/00 9:15	69:35:00	42.5	T-151	69.58	42.5	0.163		
	1/4/00 10:15	70:35:00	75.8	T-154	70.58	75.8	0.291		
	1/4/00 11:20	71:40:00	103.2	T-172	71.66	103.2	0.397		
	1/4/00 13:10	73:30:00	130.1	T-177	73.50	130.1	0.500		
	1/4/00 16:10	76:30:00	191.5	T-183	76.50	191.5	0.736		
	1/4/00 21:15	81:35:00	260.8	T-192	81.58	260.8	1.003		
	1/5/00 7:04	91:24:00	232.3	T-201	91.40	232.3	0.893		
	1/5/00 13:04	97:24:00	250.9	T-212	97.40	250.9	0.964		
	1/5/00 20:40	105:00:00	301.55	T-233	105.00	301.55	1.159	N=2	
	1/6/00 7:05	115:25:00	268.2	T-244	115.42	268.2	1.031		
	1/6/00 12:20	120:40:00	197.1	T-264	120.66	197.1	0.758		
	1/6/00 20:25	128:45:00	87.9	T-299	128.75	87.9	0.338		
	1/7/00 6:45	139:05:00	27.7	T-320	139.08	27.7	0.106		
	1/7/00 15:00	147:20:00	15.6	T-348	147.33	15.6	0.060		

U.S. EPA Denitrification Study							
Tracer Test Data, Control Cell, Level 6 (180 cm depth)							
Bromide determinations June 1997 using electrode							
Location	Time	Elapsed Time	Bromide (mg/L)	Sample ID	Time	Bromide (mg/L)	C/Co
PZ3C	1/5/00 14:30	98:50:00	0.7	T-219	98.83	0.7	0.003
	1/6/00 9:05	117:25:00	0.7	T-252	117.42	0.7	0.003
	1/8/00 12:30	120:50:00	0.8	T-271	120.83	0.8	0.003
	1/8/00 18:35	124:55:00	0.7	T-285	124.92	0.7	0.003
	1/8/00 20:35	128:55:00	0.9	T-306	128.92	0.9	0.003
	1/7/00 6:55	139:15:00	9.8	T-327	139.25	9.8	0.038
	1/7/00 11:55	144:15:00	32.3	T-337	144.25	32.3	0.124
	1/7/00 16:25	148:45:00	69.8	T-355	148.75	69.8	0.268
	1/8/00 7:30	163:50:00	202.6	T-367	163.83	202.6	0.779
	1/8/00 14:00	170:20:00	237.2	T-379	170.33	237.2	0.912
	1/8/00 21:05	177:25:00	246.8	T-391	177.42	246.8	0.949
	1/9/00 8:10	188:30:00	256.7	T-401	188.50	256.7	0.987
	1/9/00 13:45	194:05:00	228.1	T-412	194.08	228.1	0.877
	1/10/00 9:00	213:20:00	88.6	T-429	213.33	88.6	0.341
	1/10/00 15:55	220:15:00	34.1	T-439	220.25	34.1	0.131
	1/11/00 9:05	237:25:00	11.7	T-451	237.42	11.7	0.045
	1/11/00 14:00	242:20:00	8.6	T-462	242.33	8.6	0.033
	1/12/00 8:45	261:05:00	7.7	T-473	261.08	7.7	0.030
Location	Time	Elapsed Time	Bromide (mg/L)	Sample ID	Time	Bromide (mg/L)	C/Co
PZ3D	1/5/00 14:30	98:50:00	0.6	T-220	98.83	0.6	0.002
	1/6/00 9:05	117:25:00	0.6	T-253	117.42	0.6	0.002
	1/8/00 12:30	120:50:00	0.6	T-272	120.83	0.6	0.002
	1/8/00 18:35	124:55:00	1	T-286	124.92	1	0.004
	1/8/00 20:35	128:55:00	0.8	T-307	128.92	0.8	0.002
	1/7/00 6:55	139:15:00	1.2	T-328	139.25	1.2	0.005
	1/7/00 11:55	144:15:00	2.5	T-338	144.25	2.5	0.010
	1/7/00 16:25	148:45:00	3.8	T-356	148.75	3.8	0.015
	1/8/00 7:30	163:50:00	35.7	T-368	163.83	35.7	0.137
	1/8/00 14:00	170:20:00	62	T-380	170.33	62	0.238
	1/8/00 21:05	177:25:00	99.6	T-392	177.42	99.6	0.383
	1/9/00 8:10	188:30:00	173	T-402	188.50	173	0.665
	1/9/00 13:45	194:05:00	142	T-413	194.08	142	0.546
	1/10/00 9:00	213:20:00	190.1	T-430	213.33	190.1	0.731
	1/10/00 15:55	220:15:00	163.2	T-440	220.25	163.2	0.627
	1/11/00 9:05	237:25:00	70.5	T-452	237.42	70.5	0.271
	1/11/00 14:00	242:20:00	76	T-463	242.33	76	0.292
	1/12/00 8:45	261:05:00	25.1	T-474	261.08	25.1	0.096
	1/12/00 15:40	268:00:00	13.6	T-483	266.00	13.6	0.052
Location	Time	Elapsed Time	Bromide (mg/L)	Sample ID	Time	Bromide (mg/L)	C/Co
PZ3E	1/5/00 14:30	98:50:00	0.6	T-221	98.83	0.6	0.002
	1/6/00 9:05	117:25:00	0.5	T-254	117.42	0.5	0.002
	1/8/00 12:30	120:50:00	0.6	T-273	120.83	0.6	0.002
	1/8/00 14:30	122:50:00	1	T-281	122.83	1	0.004
	1/8/00 18:35	124:55:00	0.7	T-287	124.92	0.7	0.003
	1/8/00 20:35	128:55:00	0.6	T-308	128.92	0.6	0.002
	1/7/00 6:55	139:15:00	1	T-329	139.25	1	0.004
	1/7/00 11:55	144:15:00	3.5	T-339	144.25	3.5	0.013
	1/7/00 16:25	148:45:00	12.3	T-357	148.75	12.3	0.047
	1/8/00 7:30	163:50:00	180	T-369	163.83	180	0.692
	1/8/00 14:00	170:20:00	228.1	T-381	170.33	228.1	0.877
	1/8/00 21:05	177:25:00	267.1	T-393	177.42	267.1	1.027
	1/9/00 8:10	188:30:00	312.7	T-403	188.50	312.7	1.202
	1/9/00 13:45	194:05:00	267.1	T-414	194.08	267.1	1.027
	1/10/00 9:00	213:20:00	103.2	T-431	213.33	103.2	0.397
	1/10/00 15:55	220:15:00	30.4	T-441	220.25	30.4	0.117
	1/11/00 9:05	237:25:00	4.5	T-453	237.42	4.5	0.017
	1/11/00 14:00	242:20:00	1.7	T-464	242.33	1.7	0.007
	1/12/00 8:45	261:05:00	1.3	T-475	261.08	1.3	0.005

U.S. EPA Denitrification Study							
Tracer Test Data, Nitrate Cell, Level 2 (60 cm depth)							
Bromide determinations June 1997 using electrode							
Location	Time	Elapsed Time	Br (mg/L)	Sample ID	Time	Br (mg/L)	C/Co
PZ4C	1/1/00 12:50	1:10:00	0.4	T-10	1.17	0.4	0.002
	1/1/00 15:25	3:45:00	11.8	T-22	3.75	11.8	0.045
	1/1/00 22:50	11:10:00	246.7	T-34	11.17	246.7	0.949
	1/2/00 5:48	18:08:00	256.5	T-46	18.13	256.5	0.986
	1/2/00 11:07	23:27:00	256.5	T-58	23.45	256.5	0.986
	1/2/00 16:00	28:20:00	256.5	T-68	28.33	256.5	0.986
	1/2/00 23:10	35:30:00	260.8	T-80	35.50	260.8	1.003
	1/3/00 6:25	42:45:00	260.8	T-94	42.75	260.8	1.003
	1/3/00 11:15	47:35:00	260.8	T-104	47.58	260.8	1.003
	1/3/00 16:00	52:20:00	140.6	T-119	49.33	140.6	0.541
	1/3/00 21:00	57:20:00	12.8	T-129	57.33	12.8	0.049
	1/4/00 11:15	71:35:00	1	T-165	71.58	1	0.004
Location	Time	Elapsed Time	Br (mg/L)	Sample ID	Time	Br (mg/L)	C/Co
PZ4D	1/1/00 12:50	1:10:00	0.6	T-11	1.17	0.6	0.002
	1/1/00 15:25	3:45:00	31.3	T-23	3.75	31.3	0.120
	1/1/00 22:50	11:10:00	246.7	T-35	11.17	246.7	0.949
	1/2/00 5:49	18:09:00	256.5	T-47	18.15	256.5	0.986
	1/2/00 11:08	23:28:00	256.5	T-59	23.47	256.5	0.986
	1/2/00 16:00	28:20:00	256.5	T-69	28.33	256.5	0.986
	1/2/00 23:10	35:30:00	260.8	T-81	35.50	260.8	1.003
	1/3/00 6:25	42:45:00	260.8	T-95	42.75	260.8	1.003
	1/3/00 11:15	47:35:00	260.8	T-105	47.58	260.8	1.003
	1/3/00 16:00	52:20:00	45.9	T-120	49.33	45.9	0.176
	1/3/00 21:00	57:20:00	3.9	T-130	57.33	3.9	0.015
	1/4/00 11:15	71:35:00	1	T-166	71.58	1	0.004
Location	Time	Elapsed Time	Br (mg/L)	Sample ID	Time	Br (mg/L)	C/Co
PZ4E	1/1/00 12:52	1:12:00	2	T-12	1.20	2	0.008
	1/1/00 15:25	3:45:00	154.6	T-24	3.75	154.6	0.594
	1/1/00 22:50	11:10:00	228.2	T-36	11.17	228.2	0.877
	1/2/00 5:50	18:10:00	237.3	T-48	18.17	237.3	0.912
	1/2/00 11:09	23:29:00	237.3	T-60	23.48	237.3	0.912
	1/2/00 16:00	28:20:00	246.7	T-70	28.33	246.7	0.949
	1/2/00 23:10	35:30:00	250.9	T-82	35.50	250.9	0.965
	1/3/00 6:25	42:45:00	250.9	T-96	42.75	250.9	0.965
	1/3/00 11:15	47:35:00	250.9	T-106	47.42	250.9	0.965
	1/3/00 12:55	49:15:00	177.2	T-110	49.25	177.2	0.681
	1/3/00 16:00	52:20:00	64.9	T-121	52.33	64.9	0.250
	1/3/00 21:00	57:20:00	40.9	T-131	57.33	40.9	0.157
	1/4/00 11:15	71:35:00	13.3	T-167	71.58	13.3	0.051

U.S. EPA Denitrification Study							
Tracer Test Data, Nitrate Cell, Level 4 (120 cm depth)							
Bromide determinations June 1997 using electrode							
Note: No data from PZ4E.							
Location	Time	Elapsed Time	Bromide (mg/L)	Sample ID	Time	Bromide (mg/L)	C/Co
PZ4C	1/3/00 21:10	57:30:00	0.6	T-139	57.50	0.6	0.002
	1/4/00 6:15	66:35:00	0.9	T-148	66.58	0.9	0.003
	1/4/00 11:25	71:45:00	1.1	T-175	71.75	1.1	0.004
	1/4/00 16:10	76:30:00	1.2	T-186	76.50	1.2	0.005
	1/4/00 21:15	81:35:00	3.6	T-195	81.58	3.6	0.014
	1/5/00 7:07	91:27:00	146.1	T-204	91.45	146.1	0.562
	1/5/00 13:07	97:27:00	260.8	T-215	97.45	260.8	1.003
	1/5/00 20:40	105:00:00	289.6	T-236	105.00	289.6	1.114
	1/6/00 7:10	115:30:00	229.9	T-247	115.50	229.9	0.884
	1/6/00 12:25	120:45:00	115.1	T-267	120.75	115.1	0.443
	1/6/00 20:30	128:50:00	15.6	T-302	128.83	15.6	0.060
	1/7/00 6:50	139:10:00	1.5	T-323	139.16	1.5	0.006
	1/7/00 15:00	147:20:00	0.7	T-351	147.33	0.7	0.003
	1/9/00 13:55	194:15:00	0.6	T-421	194.25	0.6	0.002
	1/13/00 11:00	287:20:00	0.7	T-492	287.33	0.7	0.003
Location	Time	Elapsed Time	Bromide (mg/L)	Sample ID	Time	Bromide (mg/L)	C/Co
PZ4D	1/3/00 21:10	57:30:00	4	T-140	57.50	4	0.015
	1/4/00 6:15	66:35:00	99.3	T-149	66.58	99.3	0.382
	1/4/00 9:20	69:40:00	125.2	T-153	69.66	125.2	0.481
	1/4/00 10:15	70:35:00	130.1	T-155	70.58	130.1	0.500
	1/4/00 11:25	71:45:00	151.9	T-176	71.75	151.9	0.584
	1/4/00 13:10	73:30:00	184.2	T-178	73.50	184.2	0.708
	1/4/00 16:10	76:30:00	260.8	T-187	76.50	260.8	1.003
	1/4/00 21:15	81:35:00	281.7	T-196	81.58	281.7	1.083
	1/5/00 7:08	91:28:00	281.7	T-205	91.47	281.7	1.083
	1/5/00 13:08	97:28:00	292.8	T-216	97.47	292.8	1.126
	1/5/00 20:40	105:00:00	258.1	T-237	105.00	258.1	0.992
	1/6/00 7:10	115:30:00	47.5	T-248	115.50	47.5	0.183
	1/6/00 12:25	120:45:00	11.9	T-268	120.75	11.9	0.046
	1/6/00 20:30	128:50:00	2.1	T-303	128.50	2.1	0.008
	1/7/00 6:50	139:10:00	0.7	T-324	139.17	0.7	0.003
	1/7/00 15:00	147:20:00	0.6	T-352	147.33	0.6	0.002

U.S. EPA Denitrification Study							
Tracer Test Data, Nitrate Cell, Level 6 (180 cm depth)							
Bromide determinations June 1997 using electrode							
Co= 260.06 mg/L							
Elapsed							
Location	Time	Time	Bromide	Sample ID	Time	Bromide	C/Co
		(hr:min)	(mg/L)		(hr)	(mg/L)	
	1/1/00 11:40						
PZ4A	1/5/00 14:30	98:50:00	0.6	T-222	98.83	0.6	0.002
	1/6/00 9:10	117:30:00	0.6	T-255	117.50	0.5	0.002
	1/6/00 12:40	121:00:00	0.6	T-274	121.00	0.6	0.002
	1/6/00 16:40	125:00:00	0.6	T-288	125.00	0.6	0.002
	1/6/00 20:40	129:00:00	0.7	T-309	129.00	0.7	0.003
	1/7/00 7:00	139:20:00	0.7	T-330	139.33	0.7	0.003
	1/7/00 12:00	144:20:00	0.8	T-340	144.33	0.8	0.003
	1/7/00 16:30	148:50:00	0.7	T-358	148.83	0.7	0.003
	1/8/00 7:30	163:50:00	0.9	T-370	163.83	0.9	0.003
	1/8/00 14:00	170:20:00	0.9	T-382	170.33	0.9	0.003
	1/8/00 21:05	177:25:00	1.2	T-394	177.42	1.2	0.005
	1/9/00 8:10	188:30:00	1.2	T-404	188.50	1.2	0.005
	1/9/00 13:50	194:10:00	1.1	T-415	194.08	1.1	0.004
	1/10/00 9:00	213:20:00	3.9	T-432	213.33	3.9	0.015
	1/10/00 15:55	220:15:00	1	T-442	220.25	1	0.004
	1/11/00 9:10	237:30:00	1.9	T-454	237.50	1.9	0.007
	1/11/00 14:05	242:25:00	3.5	T-465	242.42	3.5	0.013
	1/12/00 8:45	261:05:00	36.8	T-476	261.08	36.8	0.142
	1/12/00 15:40	268:00:00	58.2	T-484	268.00	58.2	0.224
	1/13/00 11:00	287:20:00	120.2	T-493	287.33	120.2	0.462
	1/15/00 9:30	333:50:00	213.1	T-499	333.83	213.1	0.819
	1/15/00 13:30	337:50:00	205.2	T-502	337.83	205.2	0.789
	1/16/00 9:00	357:20:00	176.1	T-503	357.33	176.1	0.677
	1/16/00 16:20	364:40:00	145.5	T-504	364.67	145.5	0.559
	1/17/00 13:30	385:50:00	95.6	T-505	385.83	95.6	0.368
Location	Time	Elapsed Time	Bromide (mg/L)	Sample ID	Time	Bromide (mg/L)	C/Co
PZ4B	1/5/00 14:30	98:50:00	0.5	T-223	98.83	0.5	0.002
	1/6/00 9:10	117:30:00	0.8	T-256	117.50	0.8	0.003
	1/6/00 12:40	121:00:00	0.5	T-275	121.00	0.5	0.002
	1/6/00 16:40	125:00:00	0.5	T-289	125.00	0.5	0.002
	1/6/00 20:40	129:00:00	0.6	T-310	129.00	0.6	0.002
	1/7/00 7:00	139:20:00	1	T-331	139.33	1	0.004
	1/7/00 12:00	144:20:00	3.6	T-341	144.33	3.6	0.014
	1/7/00 16:30	148:50:00	8	T-359	148.83	8	0.031
	1/8/00 7:30	163:50:00	166.3	T-371	163.83	166.3	0.639
	1/8/00 14:00	170:20:00	210.8	T-383	170.33	210.8	0.811
	1/8/00 21:05	177:25:00	289	T-395	177.42	289	1.111
	1/9/00 8:10	188:30:00	277.8	T-405	188.50	277.8	1.068

U.S. EPA Denitrification Study								
Tracer Test Data, Nitrate Cell, Level 6 (180 cm depth)								
Bromide determinations June 1997 using electrode								
	1/9/00 13:50	194:10:00	246.8	T-416		194.08	246.8	0.949
	1/10/00 9:00	213:20:00	20.8	T-433		213.33	20.8	0.080
	1/10/00 15:55	220:15:00	1.5	T-443		220.25	1.5	0.006
	1/11/00 9:10	237:30:00	0.9	T-455		237.50	0.9	0.003
	1/11/00 14:05	242:25:00	1.1	T-466		242.42	1.1	0.004
	1/12/00 8:45	261:05:00	1.2	T-477		261.08	1.2	0.005
	1/12/00 15:40	268:00:00	1.1	T-485		268.00	1.1	0.004
Location	Time	Elapsed Time	Bromide (mg/L)	Sample ID		Time	Bromide (mg/L)	C/Co
PZ4C	1/5/00 14:30	98:50:00	0.5	T-224		98.83	0.5	0.002
	1/6/00 9:10	117:30:00	0.7	T-257		117.50	0.7	0.003
	1/6/00 12:40	121:00:00	0.6	T-276		121.00	0.6	0.002
	1/6/00 16:40	125:00:00	0.7	T-290		125.00	0.7	0.003
	1/6/00 20:40	129:00:00	1.1	T-311		129.00	1.1	0.004
	1/7/00 7:00	139:20:00	0.7	T-332		139.33	0.7	0.003
	1/7/00 12:00	144:20:00	1.1	T-342		144.33	1.1	0.004
	1/7/00 16:30	148:50:00	0.7	T-360		148.83	0.7	0.003
	1/8/00 7:30	163:50:00	4.1	T-372		163.83	4.1	0.016
	1/8/00 14:00	170:20:00	12.8	T-384		170.33	12.8	0.049
	1/8/00 21:05	177:25:00	53	T-396		177.42	53	0.204
	1/9/00 8:10	188:30:00	88.5	T-406		188.50	88.5	0.340
	1/9/00 13:50	194:10:00	147.8	T-417		194.08	147.8	0.568
	1/10/00 9:00	213:20:00	62.8	T-434		213.33	62.8	0.241
	1/10/00 15:55	220:15:00	76	T-444		220.25	76	0.292
	1/11/00 9:10	237:30:00	115.7	T-456		237.50	115.7	0.445
	1/11/00 14:05	242:25:00	111.4	T-467		242.42	111.4	0.428
	1/12/00 8:45	261:05:00	65.3	T-478		261.08	65.3	0.251
	1/12/00 15:40	268:00:00	56	T-486		268.00	56	0.215
	1/13/00 11:00	287:20:00	23.3	T-494		287.33	23.3	0.090
	1/15/00 9:30	333:50:00	14.2	T-500		333.83	14.2	0.055
	1/17/00 13:30	385:50:00	1.9	T-506		385.83	1.9	0.007
Location	Time	Elapsed Time	Bromide (mg/L)	Sample ID		Time	Bromide (mg/L)	C/Co
PZ4D	1/5/00 14:30	98:50:00	0.5	T-225		98.83	0.5	0.002
	1/6/00 9:10	117:30:00	0.5	T-258		117.50	0.5	0.002
	1/6/00 12:40	121:00:00	0.5	T-277		121.00	0.5	0.002
	1/6/00 16:40	125:00:00	0.5	T-291		125.00	0.5	0.002
	1/6/00 20:40	129:00:00	0.6	T-312		129.00	0.6	0.002
	1/7/00 7:00	139:20:00	0.5	T-333		139.33	0.5	0.002
	1/7/00 12:00	144:20:00	0.7	T-343		144.33	0.7	0.003
	1/7/00 16:30	148:50:00	0.6	T-361		148.83	0.6	0.002
	1/8/00 7:30	163:50:00	0.9	T-373		163.83	0.9	0.003
	1/8/00 14:00	170:20:00	0.8	T-385		170.33	0.8	0.003

U.S. EPA Denitrification Study								
Tracer Test Data, Nitrate Cell, Level 6 (180 cm depth)								
Bromide determinations June 1997 using electrode								
	1/8/00 21:05	177:25:00	2.3	T-397		177.42	2.3	0.009
	1/9/00 8:10	188:30:00	7.4	T-407		188.50	7.4	0.028
	1/9/00 13:50	194:10:00	49	T-418		194.08	49	0.188
	1/10/00 9:00	213:20:00	107.2	T-435		213.33	107.2	0.412
	1/10/00 15:55	220:15:00	145.5	T-445		220.25	145.5	0.559
	1/11/00 9:10	237:30:00	205.5	T-457		237.50	205.5	0.790
	1/11/00 14:05	242:25:00	213.1	T-468		242.42	213.1	0.819
	1/12/00 8:45	261:05:00	163.2	T-479		261.08	163.2	0.628
	1/12/00 15:40	268:00:00	163.2	T-487		268.00	163.2	0.628
	1/13/00 11:05	287:25:00	145.2	T-495		287.42	145.2	0.558
	1/15/00 9:30	333:50:00	34.1	T-501		333.83	34.1	0.131
	1/17/00 13:30	385:50:00	5.9	T-507		385.83	5.9	0.023
Location	Time	Elapsed Time	Bromide (mg/L)	Sample ID	Time	Bromide (mg/L)	C/Co	
PZ4E	1/5/00 14:30	98:50:00	0.6	T-226	98.83	0.6	0.002	
	1/6/00 9:10	117:30:00	175.7	T-259	117.50	175.7	0.676	
	1/6/00 12:40	121:00:00	204.9	T-278	121.00	204.9	0.788	
	1/6/00 14:30	122:50:00	221.3	T-282	122.83	221.3	0.851	
	1/6/00 16:40	125:00:00	239	T-292	125.00	239	0.919	
	1/6/00 20:40	129:00:00	258.1	T-313	129.00	258.1	0.992	
	1/7/00 7:00	139:20:00	268.2	T-334	139.33	268.2	1.031	
	1/7/00 12:00	144:20:00	277.8	T-344	144.33	277.8	1.068	
	1/7/00 16:30	148:50:00	289	T-362	148.83	289	1.111	
	1/8/00 7:30	163:50:00	78.6	T-374	163.83	78.6	0.302	
	1/8/00 14:00	170:20:00	55.1	T-386	170.33	55.1	0.212	
	1/8/00 21:05	177:25:00	24.1	T-398	177.42	24.1	0.093	
	1/9/00 8:10	188:30:00	5.2	T-408	188.50	5.2	0.020	
	1/9/00 13:50	194:10:00	3.5	T-419	194.08	3.5	0.013	
	1/10/00 9:00	213:20:00	0.7	T-436	213.33	0.7	0.003	
	1/10/00 15:55	220:15:00	1.1	T-446	220.25	1.1	0.004	
	1/11/00 9:10	237:30:00	1.2	T-458	237.50	1.2	0.005	
	1/12/00 8:45	261:05:00	1.1	T-480	261.08	1.1	0.004	