

FIELD STUDIES OF BTEX AND MTBE INTRINSIC BIOREMEDIATION

Health and Environmental Sciences Department
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Field Studies of BTEX and MTBE Intrinsic Bioremediation

Health and Environmental Sciences Department

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ABSTRACT

In the last several years, there has been considerable interest in confirming the biodegradation of soluble gasoline constituents in groundwater. Recent acceptance of risk-based approaches to corrective action has accelerated the need to better understand the role biodegradation can play in limiting the transport of and possible exposure to dissolved hydrocarbons in groundwater. This study was initiated to document the *in situ* natural biodegradation (commonly referred to as intrinsic bioremediation) of benzene; ethylbenzene; toluene; o-, m-, and p-xylene; and methyl tert-butyl ether. A rural North Carolina underground storage tank release site was selected for study. The site was instrumented with more than 50 observation wells monitored for several years to allow quantitative characterization of the downgradient mass transport of the dissolved compounds. Companion laboratory and modeling studies were conducted to facilitate interpretation of the field data.

Three dimensional field monitoring of the dissolved gasoline plume showed rapid decay of toluene and ethylbenzene during downgradient transport with slower decay of xylenes, benzene, and MTBE under mixed aerobic-denitrifying conditions. Background dissolved oxygen concentrations range from 7 to 8 mg/L, and nitrate concentrations range from 7 to 17 mg/L as Nitrogen (N) because of extensive fertilization of fields surrounding the spill.

Sampling results indicate that the plume is not growing and has reached a pseudo-steady-state. Field-scale decay rates were determined by estimating the mass flux of contaminants across four plume cross-sections. First-order decay rates for all compounds were highest near the source and lower farther downgradient. Effective first-order decay rates varied from 0 to 0.0010 d⁻¹ for MTBE; 0.0006 to 0.0014 d⁻¹ for benzene; 0.0005 to 0.0063 d⁻¹ for toluene; 0.0008 to 0.0058 d⁻¹ for ethylbenzene; 0.0012 to 0.0035 d⁻¹ for m-, p-xylene; and 0.0007 to 0.0017 d⁻¹ for o-xylene. In a companion study, laboratory microcosm studies confirmed MTBE biodegradation under aerobic conditions; however, the extent of biodegradation was limited.

BIOPLUME II and a 3-D analytical model were evaluated for their ability to simulate the transport and biodegradation of MTBE and BTEX at the site. Neither model could accurately simulate contaminant concentrations throughout the length of the plume.

TABLE OF CONTENTS

<u>Chapter</u>	<u>Page</u>
EXECUTIVE SUMMARY	ES-1
1. INTRODUCTION	1-1
1.1. INTRODUCTION.....	1-1
1.2. BTEX BIODEGRADATION	1-1
1.3. MTBE BIODEGRADATION	1-4
1.4. RESEARCH OBJECTIVES	1-5
2. SITE DESCRIPTION	2-1
2.1. BACKGROUND.....	2-1
2.2. GEOLOGIC SETTING.....	2-4
2.3. SITE HYDROGEOLOGY	2-4
3. ANALYTICAL AND FIELD METHODS	3-1
3.1. MONITORING WELL CONSTRUCTION.....	3-1
3.2. MONITORING WELL LOCATIONS.....	3-1
3.3. GROUNDWATER SAMPLING	3-3
3.4. LABORATORY ANALYTICAL METHODS.....	3-5
4. SPATIAL DISTRIBUTION OF BTEX AND INDICATOR PARAMETERS	4-1
4.1. GEOCHEMICAL INDICATOR PARAMETERS	4-1
4.2. VARIATION OF BTEX WITH TIME.....	4-2
4.3. HORIZONTAL AND VERTICAL DISTRIBUTION OF CHLORIDE, OXYGEN, NITRATE, AND INORGANIC CARBON	4-4
4.4. HORIZONTAL AND VERTICAL DISTRIBUTION OF MTBE AND BTEX.....	4-11
4.5. DISCUSSION OF FIELD MONITORING RESULTS.....	4-19
5. MASS FLUX ESTIMATION OF CONTAMINANT DEGRADATION RATES	5-1
5.1. MASS FLUX ESTIMATION.....	5-1
5.2. VARIATION IN MTBE AND BTEX MASS FLUX WITH TIME.....	5-4

5.3. VARIATION IN MTBE AND BTEX MASS FLUX WITH DISTANCE	5-8
5.4. DISCUSSION OF MASS FLUX RESULTS.....	5-15
6. MODELING STUDIES	6-1
6.1. MODEL DESCRIPTIONS	6-1
6.2. SIMULATION OF MTBE TRANSPORT AND BIODEGRADATION.....	6-3
6.2.1. BIOPLUME II Results.....	6-3
6.2.2. 3-D Analytical Solution Results.....	6-8
6.2.3. Comparison Of MTBE Simulation Results Using Bioplume II And The 3-D Analytical Solution.....	6-11
6.3. SIMULATION OF BTEX TRANSPORT AND BIODEGRADATION	6-11
6.3.1. BIOPLUME II Results For Total BTEX.....	6-11
6.3.2. 3-D Analytical Solution Results For Total BTEX And Individual Compounds	6-14
6.4. MODEL COMPARISON	6-16
7. SUMMARY AND CONCLUSIONS	7-1
REFERENCES.....	R-1

APPENDICES

A. HYDROGEOLOGIC DATA	A-1
B. FIELD SAMPLING DATA	B-1
C. MODELING WITH BIOPLUME II	C-1
D. MODELING WITH THE ANALYTICAL SOLUTION	D-1

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
ES-1.	Schematic Representation of Part of the Site's Monitoring Well..... ES-3
2-1.	Site Map Showing Major Features, Monitoring Well Locations, and Approximate Horizontal Plume Centerline (A-A') 2-2
2-2.	Cross Section along Line A-A' from Figure 2-1 Showing Screened Intervals and Approximate Vertical Plume Centerline (B-B')..... 2-3
2-3.	MTBE Breakthrough at the Most Downgradient Wells for Various Groundwater Velocities..... 2-7
3-1.	Monitoring Well Location Map 3-2
4-1.	Variation in Total BTEX Concentration with Time and Water Table Elevation in (A) MW-3s and in (B) MW-11m and MW-12m (Julian Day 0 = 1/1/92) 4-3
4-2.	Variation in MTBE and BTEX Components with Time in MW-17m (Julian Day 0 = 1/1/92)..... 4-5
4-3.	April 1, 1995, Chloride Concentration Distribution (mg/L): Plan and Profile Views 4-6
4-4.	April 1, 1995, Dissolved Oxygen Concentration Distribution (mg/L): Plan and Profile Views..... 4-7
4-5.	April 1, 1995, Nitrate Concentration Distribution (mg/L): Plan and Profile Views 4-8
4-6.	April 1, 1995, Carbon Dioxide Concentration Distribution (mg/L): Plan and Profile Views..... 4-9
4-7.	April 1, 1995, MTBE Concentration Distribution (µg/L): Plan and Profile Views 4-12
4-8.	April 1, 1995, Benzene Concentration Distribution (µg/L): Plan and Profile Views 4-13
4-9.	April 1, 1995, Toluene Concentration Distribution (µg/L): Plan and Profile Views 4-14

4-10.	April 1, 1995, Ethylbenzene Concentration Distribution ($\mu\text{g/L}$): Plan and Profile Views	4-15
4-11.	April 1, 1995, m-, p-Xylene Concentration Distribution ($\mu\text{g/L}$): Plan and Profile Views	4-16
4-12.	April 1, 1995, o-Xylene Concentration Distribution ($\mu\text{g/L}$): Plan and Profile Views	4-17
4-13.	Proportion of BTEX Compounds in Each Cross Section of the Most Contaminated Well for the April 1995 Sampling Event	4-20
5-1.	Theissen Polygon Plot for Cross-Section B Showing Ten Polygons Used to Calculate Contaminant Mass Flux	5-3
5-2.	MTBE, Benzene, Toluene, Ethylbenzene, m-, p-Xylene, and o-Xylene Mass Flux Versus Time at Lines A and B (Julian day 0 = 1/1/92)	5-6
5-3.	MTBE, Benzene, Toluene, Ethylbenzene, m-, p-Xylene, and o-Xylene Mass Flux Versus Time at Lines C and D (Julian day 0 = 1/1/92)	5-7
5-4.	MTBE and Benzene Mass Flux Versus Distance from the Source (Line A) for 1994–95.	5-9
5-5.	Toluene and Ethylbenzene Mass Flux Versus Distance from the Source (Line A) for 1994–95.	5-10
5-6.	m-, p-Xylene and o-Xylene Mass Flux Versus Distance from the Source (Line A) for 1994–95.	5-11
5-7.	Total BTEX Mass Flux Versus Distance from the Source (Line A) for 1994–95.	5-12
6-1.	Location of Monitoring Wells in the BIOPLUME II Grid.....	6-4
6-2.	Calibration of Transverse Dispersivity with Chloride in BIOPLUME II for Well Line C.	6-6
6-3.	Calibration of Transverse Dispersivity with Chloride in BIOPLUME II for Well Line D.	6-6
6-4.	Calibration of Transverse Dispersivity with MTBE in BIOPLUME II for Well Line C.....	6-7

6-5.	Calibration of Transverse Dispersivity with MTBE in BIOPLUME II for Well Line D.....	6-7
6-6.	Centerline Concentrations of MTBE as Predicted by BIOPLUME II.	6-8
6-7.	Decay Rate Calibration to Each Line of Wells: Centerline Concentrations of MTBE.....	6-10
6-8.	Model Comparison with Depth-Averaged Centerline Concentrations of MTBE.....	6-12
6-9.	Centerline Concentrations of Total BTEX as Predicted by BIOPLUME II.	6-13
6-10.	Model Comparison with Depth-Averaged Centerline Concentrations of Total BTEX.	6-17

LIST OF TABLES

<u>Table</u>		<u>Page</u>
ES-1.	Biodegradation of BTEX and MTBE Expressed as First- Order Decay Rate Constants.....	ES-6
3-1.	Sample Collection and Preparation Protocol	3-4
4-1.	Average Peak Concentrations Observed in Well Lines A, B, C, and D for the 1994–95 Monitoring Period	4-18
5-1.	Fraction of Mass Flux at Line A	5-13
5-2.	Effective First-Order Decay Rates from Mass Flux Analysis.....	5-14
6-1.	First-Order Decay Rates for MTBE Using the 3-D Analytical Solution by Domenico	6-9
6-2.	First-Order Decay Rates for BTEX Using the 3-D Analytical Solution by Domenico	6-15
7-1.	Summary First-Order Decay Rates Using Mass Flux Approach.....	7-2

EXECUTIVE SUMMARY

Gasoline contains the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylene isomers (BTEX). Oxygenates such as methyl tert-butyl ether (MTBE) are often used in gasoline for octane enhancement and reducing vehicular emissions. These compounds are water soluble and potentially toxic at high concentrations, and are the indicator compounds targeted for remediation when gasoline releases to groundwater occur. Cleanup requirements for benzene are typically more stringent than for the other compounds, because the federal drinking water Maximum Contaminant Level (MCL) is 5 µg/L. There is no MCL for MTBE, but EPA has prepared several draft Health Advisories since 1993, and the suggested Lifetime Health Advisory in the most current draft is 70 µg/L (Gomez-Taylor, 1997). Because of the high costs associated with long term groundwater remediation at impacted sites, during the last several years there has been growing interest in confirming the biodegradation of soluble gasoline constituents in groundwater. Recent acceptance and increasing application of risk-based approaches to corrective action have accelerated the need to better understand the role biodegradation can play in limiting the transport of and possible exposure to dissolved hydrocarbons and oxygenates in groundwater.

An active, diverse microbial community exists in the subsurface and is capable of degrading a wide variety of hydrocarbons as well as MTBE. Factors that affect the rate and extent of biodegradation are (1) the quantity and metabolic capacity of the microorganisms; (2) the type and amount of electron acceptors present (e.g., oxygen, nitrate, ferric iron, and sulfate); (3) the quantity and quality of nutrients; (4) temperature; (5) pH; and (6) oxidation-reduction potential. If aerobic conditions exist in an aquifer, oxygen will be utilized as an electron acceptor for hydrocarbon biodegradation. Oxygen is a co-substrate for the initiation of hydrocarbon metabolism and is the preferred electron acceptor because microbes gain the most energy from aerobic reactions. Numerous studies have shown the BTEX compounds are readily biodegradable in the presence of excess oxygen (Jamison *et al.*, 1975; Gibson and Subramanian, 1984; Barker *et al.*, 1987; Wilson *et al.*, 1986; Alvarez and Vogel, 1991), and many other studies have documented BTEX biodegradation with other electron acceptors (i.e., anaerobic

biodegradation), including nitrate (Hutchins *et al.*, 1991b; Krumholz *et al.*, 1996). There are a few well-documented cases of MTBE biodegradation in the literature, Lee (1986), Jensen and Arvin (1990), Suflita and Mormile (1993), Salanitro *et al.* (1994), Yeh and Novak (1994), Barker *et al.* (1990), Hubbard *et al.* (1994). These studies show that while MTBE can be biodegraded under certain conditions, biodegradation will often be slow and may only occur under specific environmental conditions.

OBJECTIVES

The overall objective of this project was to examine the effectiveness of intrinsic bioremediation in controlling the migration of dissolved benzene; ethylbenzene; toluene; o-, m-, and p-xylene; and methyl tert-butyl ether released from a gasoline spill in Sampson County, N.C. Intrinsic bioremediation is a corrective action technology involving careful characterization and monitoring of the transport of dissolved plume constituents, and documentation of their mass loss due to biodegradation by the naturally occurring bacteria at a site - without attempting to enhance the biodegradation rate (e.g., by adding nutrients or oxygen). This technique may be used alone to contain small releases or in combination with other remediation techniques to complete aquifer restoration.

A gasoline release field site was selected, an extensive monitoring well network installed, and the site was monitored for more than three years to allow calculation of “real world” *in situ* biodegradation rates. Using aquifer materials from this site, laboratory microcosm experiments were performed to further characterize the biodegradation of BTEX and MTBE under ambient, *in situ* conditions. Finally, groundwater modeling studies were conducted to facilitate the interpretation of field data, and to evaluate various approaches for predicting the fate and transport of these gasoline constituents in the subsurface (Borden *et al.*, 1997).

SITE CHARACTERISTICS

A rural underground storage tank (UST) release site in the Coastal Plain of North Carolina was selected for study. The USTs had been removed along with some contaminated soil in the late 1980s. A detailed field characterization of the site was performed to clearly delineate the periphery of the dissolved plume emanating from the remaining residual gasoline present at and below the water table, and to identify hydrologic or geochemical conditions that might influence the rate of biodegradation. The site was instrumented with more than 50 multi-level observation wells, including four monitoring well transects each established perpendicular to the direction of groundwater flow (Figure E-1). Each transect contained up to five or six monitoring well clusters, and each of the clusters contained three wells to allow sampling at the water table, at the bottom of the aquifer, and at a point midway between. One transect was located through the source area, and the three others were established at 36 m, 88 m, and 177 m downgradient from the source. Wells at the site were sampled on a regular basis for more than three years. The mass flux of BTEX and MTBE moving through the plane of each transect could then be determined, which allowed quantitative characterization of the downgradient mass transport of these dissolved compounds (i.e., the rate of intrinsic bioremediation).

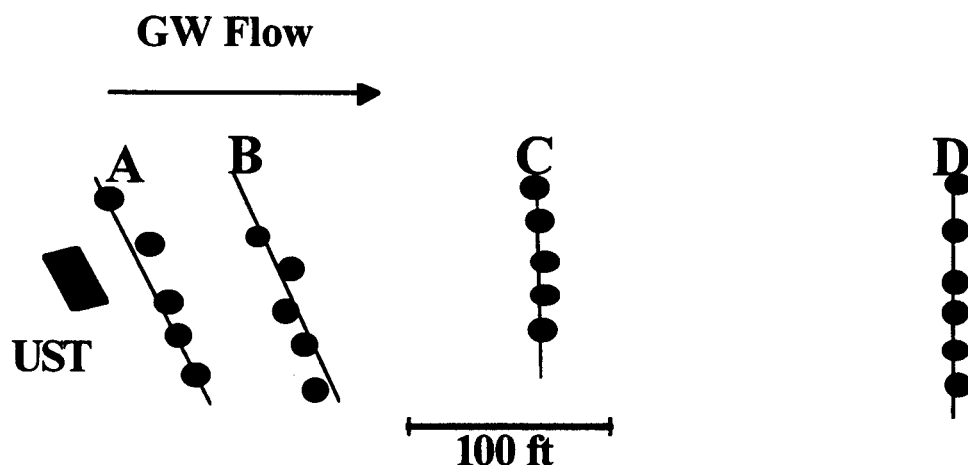


Figure ES-1. Schematic representation of part of the site's monitoring well network showing the four transects established to characterize mass flux of dissolved compounds flowing past each transect. Each circle represents a cluster of three monitoring wells completed to different depths below the water table.

The depth of the water table at the site varied seasonally between 1-3 m below the land surface, the saturated thickness averaged about 7 m. The hydraulic conductivity ranged from 0.3 to 1.1 m/d (average = 0.8 m/d), and the groundwater velocity was estimated at 4-16 m/yr, with an average of 8 m/yr. Soil organic carbon content of the aquifer material was about 0.05%. The pH of the groundwater was 4.3, background dissolved oxygen concentrations ranged from 7 to 8 mg/L, and nitrate concentrations ranged from 7 to 17 mg/L as Nitrogen (N) because of extensive fertilization of the agricultural fields surrounding the spill. Average peak concentrations of dissolved BTEX and MTBE in the source area were around 10-40 mg/L and 10 mg/L, respectively. Measurable concentrations of dissolved BTEX and MTBE present in the aquifer had migrated over 180 m from the source area before discharging to a farm field drainage ditch.

BIODEGRADATION

Significant levels of nitrate were present throughout the dissolved plume, and TEX biodegradation appeared to occur using both oxygen and nitrate as terminal electron acceptors. Dissolved oxygen (DO) concentrations within the dissolved plume were much lower than background levels. They varied from less than 0.5 mg/L in the core of the plume, to about 4-6 mg/L near the fringes. Oxidation-reduction potentials through the plume ranged from +200 to +450 mV, consistent with the dominance of nitrate serving as a redox buffer. Methane was never detected in the groundwater, but some dissolved iron and sulfate were observed in monitoring wells. However, those concentrations were generally low, and there is no evidence of significant biodegradation with subsequent reduction of iron and sulfate. The very rapid removal of toluene, ethylbenzene, and m-, p-xylenes and the much slower removal of o-xylene and benzene at this site are consistent with studies on BTEX biodegradation via denitrification reported in several recent papers (e.g., Hutchins *et al.*, 1991b). For example, over the 88 m distance from Line A to Line D, the mass flux of toluene, ethylbenzene and m-, p-xylenes decreased by 99%. Interpretation of three years of sampling results indicate that the plume is not growing and has reached a pseudo-steady-state.

Results from companion laboratory studies using (1) aerobic, (2) low initial oxygen, and (3) anaerobic-denitrifying microcosms showed no evidence of anaerobic benzene degradation, indicating mass transfer of oxygen into the plume will be the limiting factor influencing benzene biodegradation in the aquifer. Anaerobic biodegradation of TEX in the aquifer is likely enhanced by the presence of high background levels of nitrate leached from fertilizer applied to the overlying and surrounding agricultural fields. This mass loss of TEX under nitrate-reducing conditions contributes to a net decline in the plume's biological oxygen demand further downgradient, which should facilitate the availability of oxygen for aerobic biodegradation of the remaining benzene.

A mass flux calculated from the data obtained from each of the four monitoring well transects was used to estimate field-scale first-order decay rates for MTBE and BTEX. Most groundwater biodegradation models use first-order rate constants as the input data that characterize biodegradation rates. Near the source, first-order decay rate constants are highest for toluene and ethylbenzene and lowest for o-xylene, benzene, and MTBE (Table E-1). The rate constants displayed in Table E-1 are comparable to results summarized previously (Rifai *et al.*, 1995). As the dissolved plume travels downgradient, the rates of mass decay decline for all compounds, indicating that there was a substantially greater amount of biodegradation occurring in the initial 36 m downgradient from the source. The decline in the toluene and ethylbenzene decay rates may be a calculation artifact, since they were almost completely removed from the system (i.e., their concentrations were often close to the analytical detection limit at lines C and D). However, elevated (i.e., easily measurable) concentrations of o-xylene, benzene and MTBE remained at lines C and D, and the decline in their mass decay rates with distance from the source appears to be real.

The field monitoring results provide evidence of MTBE decay near the contaminant source. However, there is no evidence for MTBE decay in the downgradient aquifer. This is supported by aerobic laboratory microcosms (Borden *et al.*, 1997) that showed limited MTBE biodegradation near the source but no evidence for MTBE biodegradation further downgradient. The unusual shape of the MTBE degradation profile in laboratory microcosms suggests that one or more unknown factors are limiting or inhibiting MTBE biodegradation.

Table ES-1. Biodegradation of BTEX and MTBE Expressed as First-Order Decay Rate Constants.

Compound	Line A to B (0-36 m)	Line B to C (36-88 m)	Line C to D (88-177 m)
MTBE	0.0010	0.0008	Not Significant
Benzene	0.0014	0.0009	0.0006
Toluene	0.0063	0.0020	0.0005
Ethylbenzene	0.0058	0.0019	0.0008
m-, p-Xylene	0.0035	0.0022	0.0012
o-Xylene	0.0017	0.0010	0.0007
BTEX	0.0029	0.0010	0.0007

[Note: d^{-1} = "inverse days"; $0.0010 d^{-1}$ = 0.1% mass loss of that compound per day]

MODELING

BIOPLUME II and a 3-D analytical model (Dominico, 1987) were evaluated for their ability to simulate the transport and biodegradation of MTBE and BTEX in the shallow aquifer. In both models, MTBE biodegradation was represented by a constant first-order decay rate. As a consequence, predicted MTBE distributions using both models were very similar. Both models provided reasonable predictions of MTBE concentrations in the middle of the plume but significantly underestimated concentrations at the most downgradient wells. The poor match between predicted and observed concentrations at the most downgradient wells is primarily due to the decline in contaminant degradation rates with distance observed in the field study. Since these models use a constant decay rate, they overestimated the rate of contaminant loss in the distant portion of the plume at the field site, and therefore predicted lower contaminant concentrations than were actually present.

Chapter 1

INTRODUCTION

1.1. INTRODUCTION

One of the causes of shallow groundwater contamination is the release of gasoline into the subsurface from leaking underground storage tanks (USTs). Gasoline contains the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylene isomers (BTEX). Oxygenates such as methyl *tert*-butyl ether (MTBE) are often used in gasoline for octane enhancement and air pollution control. These compounds are water soluble and can be toxic at high concentrations. Of the compounds mentioned, benzene causes the greatest concern since it is a known human carcinogen (NIOSH, 1990).

Intrinsic bioremediation is a corrective action approach that allows indigenous microorganisms to biodegrade contaminants without human intervention. This technique may be used alone to contain small releases or in combination with other remediation techniques to complete aquifer restoration. The objective of this study is to examine the effectiveness of intrinsic bioremediation for control of BTEX and MTBE released from a gasoline spill in Sampson County, N.C.

1.2. BTEX BIODEGRADATION

An active, diverse microbial community exists in the subsurface and is capable of degrading a wide variety of hydrocarbons (Zobell, 1946; Webster *et al.*, 1985; Wilson *et al.*, 1986; Ghiorse and Wilson, 1988). Jamison *et al.* (1975) found that a mixed microbial population from a gasoline-contaminated aquifer readily degraded all gasoline components under aerobic conditions. Some hydrocarbons did not support microbial growth when present as the sole carbon source; however, all compounds were degraded when present as a mixture. This finding suggests that a mixed microbial population may be necessary for complete biodegradation of complex hydrocarbon mixtures. Ridgeway *et al.* (1990) studied microbial activity in an aquifer contaminated with unleaded gasoline. They found that most organisms were very specific in their ability to degrade hydrocarbons and were able to degrade only one of several closely related

compounds. Toluene, p-xylene, ethylbenzene, and 1,2,4-trimethylbenzene were the most frequently utilized substrates for growth, while cyclic and branched alkanes were the least frequently used. Factors that affect the rate and extent of biodegradation are (1) the quantity and metabolic capacity of the microorganisms, (2) the type and amount of electron acceptors present [O_2 , NO_3^- , SO_4^{2-} , $Fe(III)$, CO_2], (3) the quantity and quality of nutrients, (4) temperature, (5) pH, and (6) oxidation-reduction potential.

If aerobic conditions exist in an aquifer, oxygen will be utilized as an electron acceptor for hydrocarbon biodegradation. Oxygen is a co-substrate for the initiation of hydrocarbon metabolism (Young, 1984) and is the preferred electron acceptor because microbes gain the most energy from aerobic reactions. Numerous studies have shown the BTEX compounds are readily biodegradable in the presence of excess oxygen (Jamison *et al.*, 1975; Gibson and Subramanian, 1984; Barker *et al.*, 1987; Wilson *et al.*, 1986; Alvarez and Vogel, 1991). Some studies suggest that there may be a minimum level of oxygen required for aerobic biodegradation. Chiang *et al.* (1989) found that BTEX biodegradation was rapid (half-life of 5 to 20 days) when oxygen concentrations were greater than 2 mg/L, but little or no biodegradation was observed when initial oxygen concentrations were 0, 0.1, or 0.5 mg/L.

Under anaerobic conditions, toluene; ethylbenzene; and m-, p-xylene can be biodegraded using nitrate as the electron acceptor (Kuhn *et al.*, 1985; Zeyer *et al.*, 1986; Kuhn *et al.*, 1988; Hutchins, 1991a; Hutchins *et al.*, 1991b). o-Xylene has often been found to be recalcitrant under denitrifying conditions when present as a sole substrate but may be slowly biodegraded in the presence of other degradable substrates (Hutchins, 1991a; Kao and Borden, in press). Several investigators have reported that benzene is recalcitrant under denitrifying conditions (Zeyer *et al.*, 1986; Kuhn *et al.*, 1988; Hutchins, 1991a; Hutchins *et al.*, 1991b; Barbaro *et al.*, 1992), but other work indicates that benzene is biodegradable (Major *et al.*, 1988). Even though biodegradation can occur using nitrate as the terminal electron acceptor, the rate of biodegradation is often slower under denitrifying than under aerobic conditions, and there may be a significant lag period before denitrification begins (Hutchins, 1991b).

Recent work has suggested that the presence of nitrate may enhance TEX biodegradation under low oxygen, hypoxic conditions (0.1 to 2 mg/L oxygen). Using an enrichment culture technique, Mikesell *et al.* (1993) isolated a strain of *Pseudomonas fluorescens* in which growth and BTEX degradation under hypoxic conditions (2 mg/L oxygen) were enhanced by the presence of nitrate. Similarly, Hutchins *et al.* (1992) observed an increase in TEX removal from 77% to 97% in oxygen-limited columns when 10 mg/L $\text{NO}_3\text{-N}$ was added to the column influent. Throughout this experiment, an average of 0.3 mg/L dissolved oxygen (DO) was observed in the nitrate-amended column effluent. These results are somewhat surprising given past research on the effects of oxygen concentration on denitrification. Christiansen and Tiedje (1988) found that low levels of DO (0.1 to 0.4 mg/L) can significantly reduce denitrification rates (0 to 15% of control). Anoxic regions may persist in the center of soil aggregates (Sexstone *et al.*, 1985) even though the mobile pore water contains low levels of DO.

Barker *et al.* (1987) conducted a field study of aerobic BTEX biodegradation at the Canadian Forces' Base Borden, Ontario. When 1800 liters of solution containing 7.6 mg/L of BTEX were injected into the aquifer, all BTEX components were completely degraded in 1.2 years. Chiang *et al.* (1989) studied the intrinsic biodegradation of BTEX at a sandy aquifer in Michigan and showed a spatial relationship between DO and BTEX concentration. Hutchins *et al.* (1991a) stimulated the biodegradation of JP-4 jet fuel at Traverse City, Mich., under denitrifying conditions through the addition of nitrate to the aquifer. Results indicated that toluene; ethylbenzene; and m-, p-xylene were readily degradable while o-xylene was less degradable. Berry-Spark *et al.* (1986) studied the effect of nitrate addition on BTEX biodegradation. Initially, 2500 liters of solution containing 800 $\mu\text{g/L}$ of BTEX were injected into the shallow aquifer at the Canadian Forces' Base Borden. Four days after the BTEX injection, 2400 liters of solution containing 45 mg/L of NO_3^- as N were injected into the aquifer. The results suggested that nitrate may have enhanced the biodegradation of BTEX, although the results were not conclusive since all BTEX components degraded in both the nitrate-treated system and the control system.

1.3. MTBE BIODEGRADATION

There are few well-documented cases of MTBE biodegradation in the literature. Lee (1986) studied BTEX and MTBE biodegradation in soil collected from sites in Traverse City, Mich., and the Texas Gulf Coast. In studies with the Traverse City soil, 84% of MTBE was degraded after 4 weeks of aerobic incubation, but there was no apparent biodegradation of MTBE after 8 weeks of incubation at the Texas site. In studies of aerobic BTEX and MTBE biodegradation, Jensen and Arvin (1990) found no evidence of MTBE degradation after 60 days of incubation. However, BTEX biodegradation was largely unaffected by the presence of MTBE. Only at concentrations greater than 200 mg/L MTBE was there a slight inhibitory effect on BTEX biodegradation.

In an initial study, Suflita and Mormile (1993) found no evidence of MTBE degradation after 182 days of incubation under methanogenic conditions. Results from biodegradation studies using other fuel additives suggest that the chemical structure of these compounds greatly affects their susceptibility to biological decay. Compounds containing a tertiary or quaternary carbon atom, like MTBE, were more resistant to biodegradation than other unbranched or moderately branched chemicals. In more recent work, Mormile *et al.* (1994) found MTBE to be recalcitrant under methanogenic conditions in sediment from a stream, a sanitary landfill, and a gasoline-contaminated aquifer but was biodegraded in one of three replicate microcosms containing Ohio River sediment after 152 days of incubation. MTBE biodegradation in the single Ohio River microcosm was confirmed by the stoichiometric production of *tert*-butanol (TBA).

Salanitro *et al.* (1994) enriched an industrial chemical plant biotreater sludge to develop a mixed bacterial culture that rapidly biodegraded MTBE. In batch experiments, the culture degraded 120 mg/L of MTBE in 4 hours at a rate of 34 mg MTBE/g cells per hour. While none of the individual isolates could use MTBE as a sole carbon source, the culture as a whole was able to convert radiolabeled MTBE to $^{14}\text{CO}_2$ and cell mass. TBA was produced as a metabolic product of MTBE biodegradation. TBA was also degraded but at a slightly slower rate (14 mg TBA/g cells per hour) than MTBE.

Yeh and Novak (1994) provided the most substantial evidence for anaerobic degradation of MTBE. Using soils with varying natural organic contents, they evaluated the potential for MTBE biodegradation under denitrifying, sulfate reducing, and methanogenic conditions. While there was no loss of MTBE after 250 days in the organically rich soils, degradation was observed in soil with a low organic carbon content under methanogenic conditions. However, degradation occurred only when nutrient amendments were added. They hypothesized that the first and rate-limiting step in MTBE degradation may be cleavage of the ether bond, resulting in the production of TBA.

In a field experiment at the Canadian Forces' Base in Borden, Ontario, Barker *et al.* (1990) investigated the influence of MTBE on the transport and degradation of monoaromatic hydrocarbons in groundwater. The presence of MTBE had no apparent effect on the rate of migration or decay for the BTEX compounds. While the BTEX compounds were readily degraded, MTBE exhibited no mass loss over the 16-month period of the study. Using sediment from the Borden test site, Hubbard *et al.* (1994) found MTBE to be recalcitrant in both aerobic and oxygen-limited microcosms over incubation periods of 8 to 15 months. As in the field studies, biotransformation of the monoaromatics appeared to be unaffected by the presence of MTBE.

These results indicate that while MTBE can be biodegraded under certain conditions, biodegradation will often be slow and may be limited to specific environmental conditions.

1.4. RESEARCH OBJECTIVES

The overall objective of this project was to examine the effectiveness of intrinsic bioremediation in controlling the migration of dissolved BTEX and MTBE released from a gasoline spill in Sampson County, N.C. A detailed field characterization was performed to determine the rate of BTEX and MTBE biodegradation in the subsurface and to identify hydrologic or geochemical conditions that might influence the rate of biodegradation. Modeling studies were performed to evaluate various approaches for predicting the fate and transport of contaminants in the

subsurface. Laboratory microcosm experiments were also performed to document the biodegradation of BTEX and MTBE under ambient, *in situ* conditions (Borden *et al.*, accepted).

Chapter 2

SITE DESCRIPTION

2.1. BACKGROUND

This study was conducted at a gasoline spill located in Sampson County, N.C., approximately 15 miles northwest of the town of Clinton. Two USTs formerly located on the site were used to store gasoline and diesel fuel for farm and personal vehicles. A leak in the gasoline storage tank was discovered sometime in 1986 or 1987. In December 1990, both tanks were removed from the site. One 250-gallon gasoline tank and one 500-gallon diesel fuel tank were located in a single tank bed. Upon removal, the diesel tank appeared to be in good condition; however, the gasoline tank had several rusted holes on the bottom and along the seams of the tank. During tank removal, soil exhibited characteristic gasoline odors, and approximately 15 gallons of gasoline were released into the excavation from the UST. Soil samples collected from the excavation confirmed the presence of petroleum hydrocarbon compounds identified as No. 2 fuel oil and gasoline. Approximately 90 yd³ of contaminated soil were then excavated from the tank bed for off-site disposal. However, nearby buildings limited excavation, and a substantial amount of residual gasoline remains trapped in the soil below the water table and provides a continuing source of dissolved gasoline constituents to the groundwater.

From December 1990 through January 1991, 30 augured borings and 10 monitoring wells were installed to define the extent of soil and groundwater contamination (SGI Environmental Engineering Services, 1992). Results confirmed the presence of dissolved gasoline in the groundwater and its transport in a northeasterly direction. In June 1992, North Carolina State University (NCSU) initiated a study of intrinsic bioremediation processes at this site with support from the American Petroleum Institute. Since that time, a total of 56 monitoring wells were installed to delineate the horizontal and vertical extent of the plume. Soil and groundwater sampling was conducted to monitor hydrocarbon contamination and plume migration. Figure 2-1 shows the location of the former USTs and the monitoring well array that was installed. The approximate horizontal centerline of the contaminant plumes is shown as line A-A' on

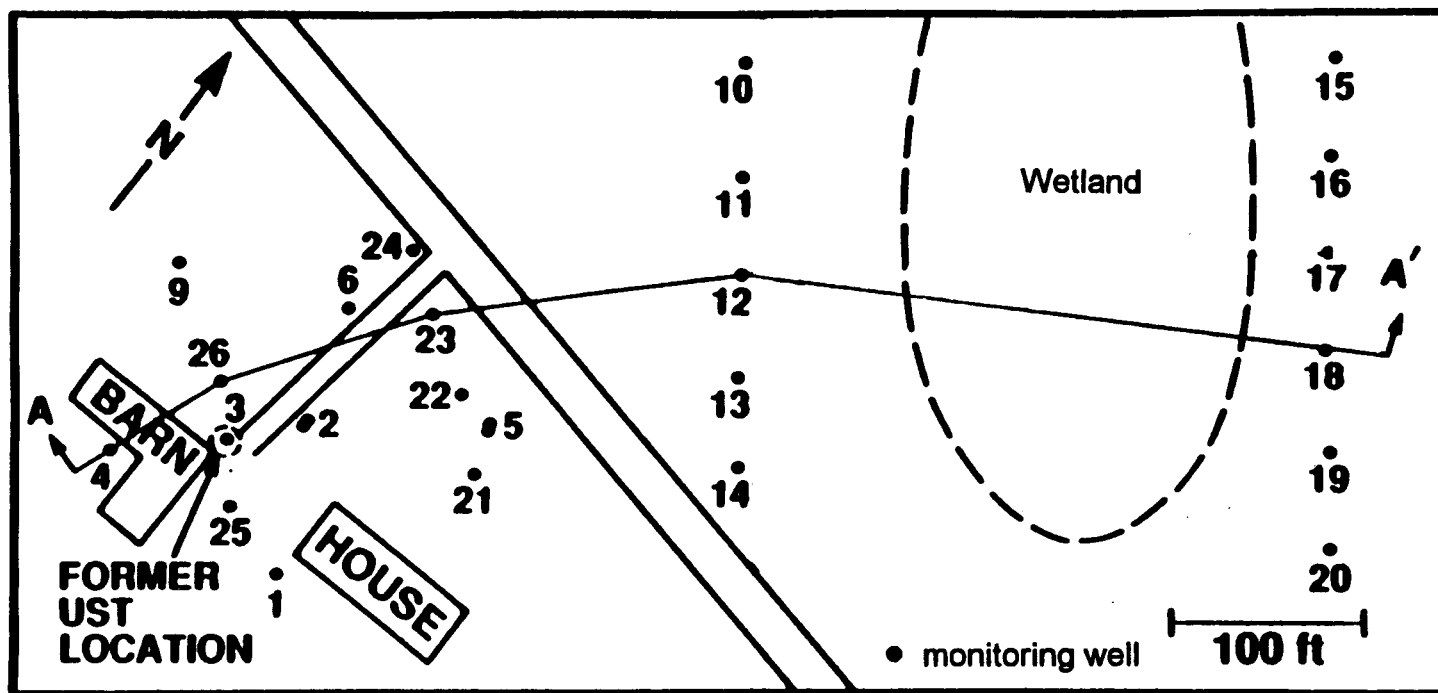


Figure 2-1. Site Map Showing Major Features, Monitoring Well Locations, and Approximate Horizontal Plume Centerline (A-A').

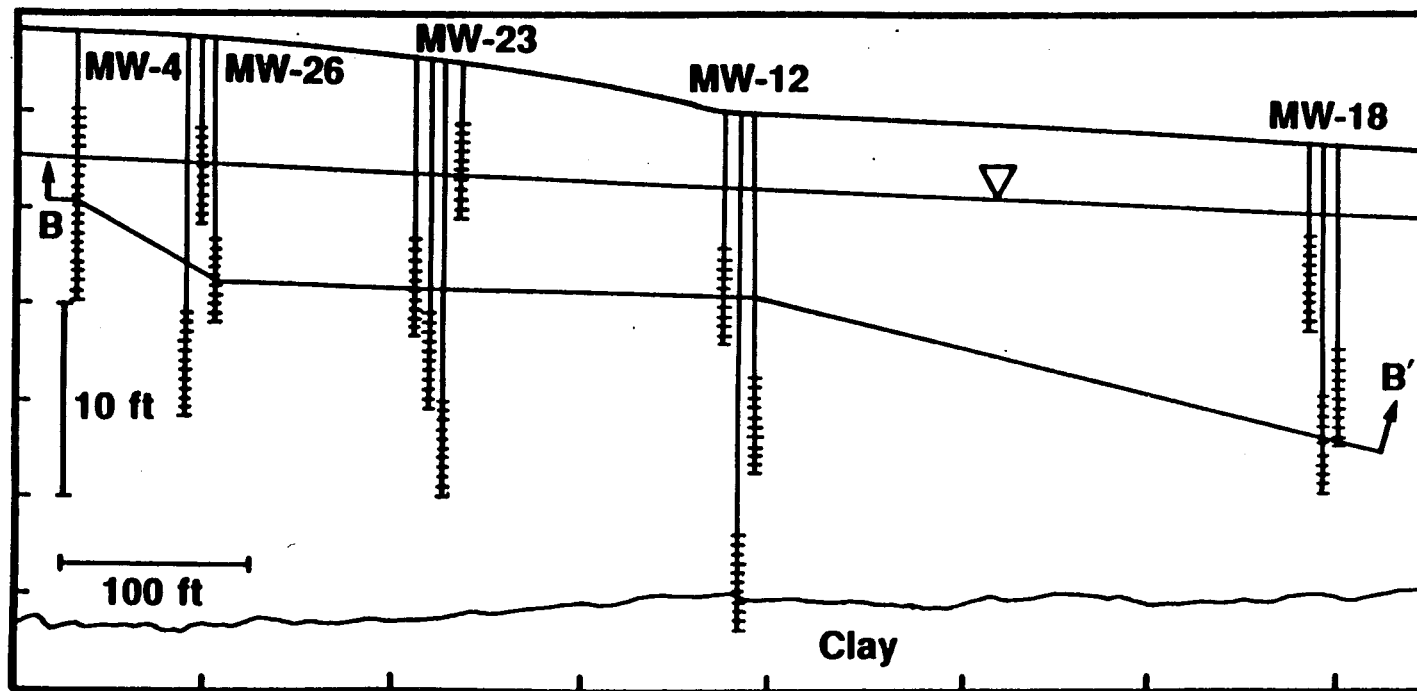


Figure 2-2. Cross Section along Line A-A' from Figure 2-1 Showing Screened Intervals and Approximate Vertical Plume Centerline (B-B').

Figure 2-1. The monitoring wells on this line are shown in the profile view in Figure 2-2. Line B-B' represents the approximate vertical centerline of the contaminant plumes.

2.2. GEOLOGIC SETTING

The Daughtry site is located in the north central portion of Sampson County in the inner Coastal Plain physiographic province. The geology of the Coastal Plain of North Carolina consists mainly of a thin layer of sands and clays beneath which lies much older formations. The topography is characterized by flat terrain dissected by tributaries and man-made drainage canals feeding small ponds and swamps.

The site geology consists mainly of red-to-rose colored clayey sands to a depth of between 1 to 10 ft. Deposits below 10 ft typically consist of layers of moderately coarse quartz sand containing yellow-to-rose colored silty material. Occasional discontinuous lenses of red plastic clay are encountered in the quartz sand. Beneath the sandy layer at a depth of 25 to 30 ft lies a heavy, tight gray-to-black lignitic clay, containing well-rounded broken shell material and medium-to-fine gravel. The overlying clayey and silty sands are believed to correlate with Quaternary surficial deposits, while the underlying organic clays are believed to correlate with the Black Creek Formation (Stephenson, 1923; Swift and Heron, 1969).

2.3. SITE HYDROGEOLOGY

A single unconfined aquifer is present throughout the site. While there are two identifiable zones in this aquifer, their permeabilities are sufficiently similar to consider them a single unit. The vertical extent of contamination will be limited by the underlying lignitic clay layer at 25 to 30 ft below grade.

Water table elevations have been measured periodically from July 1992 to April 1995. Water table contours for each sampling event are shown in Appendix A of the companion appendices document by Borden *et al.* (1997). Groundwater flow is typically to the north-northeast with minor variations. The only significant change in the flow direction occurred in July 1992. At that time, flow was almost due east. This variation could have been caused by measurement error or

the low water table position because of an extended dry period. Over a 3-week period in August 1992, approximately 12 inches of rain caused the water table to rise roughly 4 ft. This recharge event shifted the groundwater flow back to a north-northeasterly direction. Subsequent monitoring indicates that the groundwater flow is consistently to the north-northeast.

This site is located immediately adjacent to a wetland on Carolina Bay. Carolina Bay has been described by Stuckey (1965) as depressed circular to elliptical topographical scars that may contain a lake but are usually marshy or swampy (Figure 2-1). The Carolina Bay is believed to act as both a groundwater recharge and discharge area. During the winter, water collects in this area enhancing groundwater recharge. During the summer, the capillary fringe is close to the land surface in this area enhancing evapotranspiration from the water table.

Specific capacity and/or rising head slug tests were conducted on 17 wells located throughout the site. The measured hydraulic conductivity ranged from 0.9 to 3.6 ft/d with an average of 2.6 ft/d. No consistent trends in the horizontal permeability distribution could be identified from the slug and specific capacity test results. The shallow zone appears to be slightly more permeable than the lower zone, although the average permeabilities of these two layers are not statistically different. An effective porosity of 0.1 was estimated from chloride tracer tests conducted on two 18-inch by 1-inch-diameter undisturbed cores (one from shallow and one from deeper zone) and are described in detail by Daniel (1995). The effective porosities from these two tests matched within 10%. The low estimated value of effective porosity is presumably due to the broad range of grain sizes in the soil that cause bypassing of flow around the clay-rich zones.

Soil samples were analyzed for organic carbon content (f_{oc}) to better estimate the extent of sorption occurring at the site. The average soil organic carbon content (average $f_{oc}=0.0005$) was determined from analysis of three soil samples (8 and 15 ft below grade at an upgradient location and 8 ft below grade at a downgradient location) and analyzed by an independent analytical service laboratory using the high temperature UV oxidation procedure. Retardation factors for the MTBE and the BTEX components were estimated (Section 3.0 of Appendix A in Borden *et al.*, 1997) using the empirical correlation between soil partition coefficient and the octanol-water

partition coefficient developed by Schwarzenbach and Westall (1981). The calculated retardation factors were 1.003 for MTBE; 1.03 for benzene; 1.08 for toluene; 1.09 for o-xylene; 1.18 for ethylbenzene; and 1.19 for m-, p-xylene.

The time-averaged water table gradient at the site is 0.0041 ft/ft. Using the measured range of permeability, groundwater velocity was estimated to vary from 13 ft/yr to 54 ft/yr with an average of 39 ft/yr. At these velocities, a non-reactive contaminant should take between 11 and 45 years to reach the most downgradient wells. During the initial site characterization, it became apparent that the actual transport velocity must be slightly higher than the average velocity calculated above. MTBE use was not widespread until 1984. However, in Spring 1993, MTBE was already present in the most downgradient wells indicating that the actual travel time from the source was 9 years or less. To develop a more accurate estimate of the solute transport velocity, a three-dimensional analytical solution to the advection-dispersion-equation (Domenico, 1987) was fit to the MTBE monitoring results from the most downgradient wells using the calculated retardation factor for MTBE and assuming the initial MTBE release occurred in 1984. Observed MTBE concentrations in the most downgradient well are compared to model predictions for several different transport velocities in Figure 2-3. The results from this analysis suggest that the average transport velocity at the site is approximately 57 ft/yr.

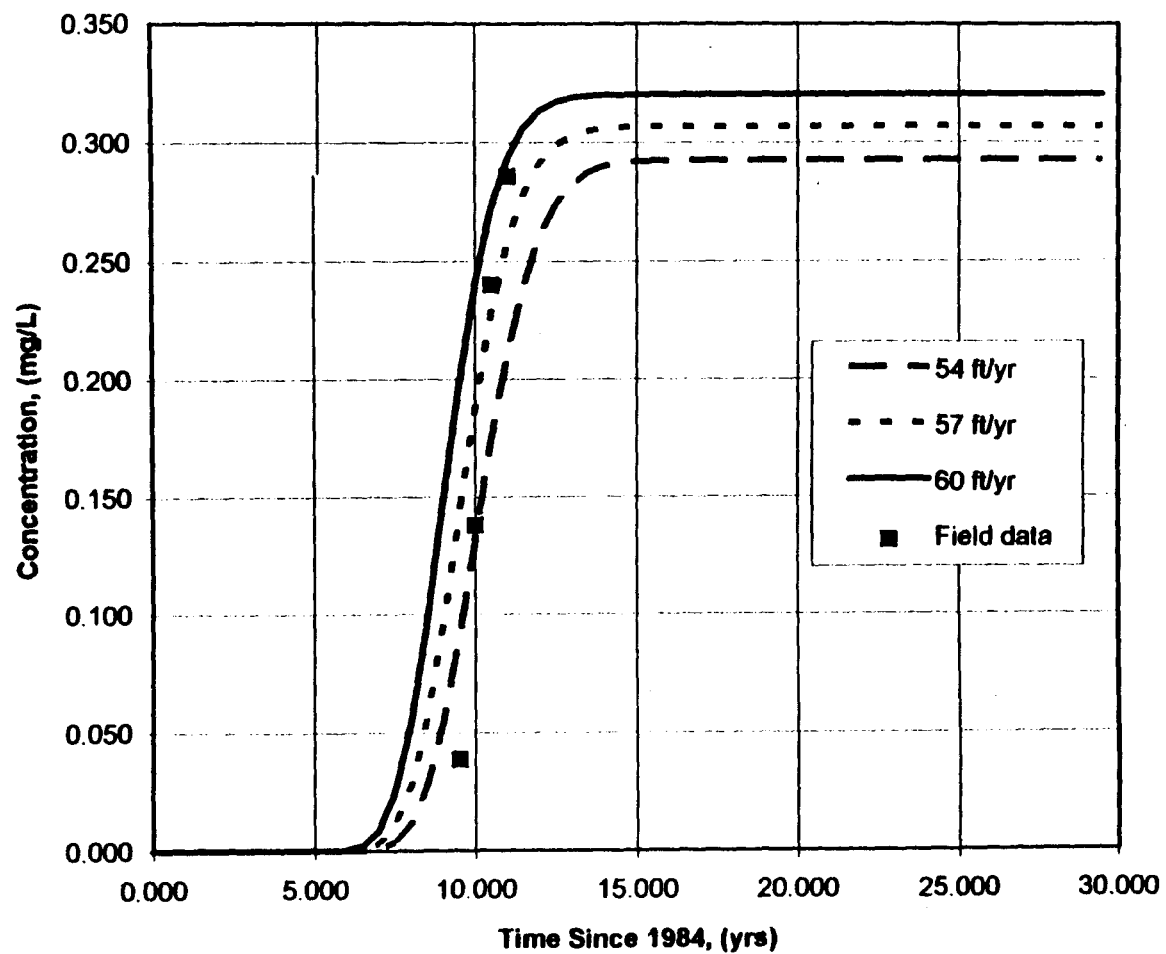


Figure 2-3. MTBE Breakthrough at the Most Downgradient Wells for Various Groundwater Velocities.

Chapter 3

ANALYTICAL AND FIELD METHODS

3.1. MONITORING WELL CONSTRUCTION

The monitoring wells installed at the Sampson County, N.C., site were constructed in accordance with the Well Construction Standards, Subpart 2c, Section .0108, of the N.C. Administrative Code, Title 15 of the Department of Environmental Health and Natural Resources, Division of Environmental Management. NCSU did not install monitoring wells 1, 2, 2D, 3, 4, 5, 6, and 9.

The installation of a monitoring well required the advancement of a 5.25-inch-diam. hole not less than 1.0 ft deeper than the maximum depth of the well. Monitoring wells were constructed of 2.0-inch-diam. PVC well casing with a 5.0-ft-long, 0.01 in. (10 slot) PVC screen and accompanying end plug. A natural sand pack was placed around the screened interval of the well casing and a Bentonite pellet seal was installed above the sand pack to prevent the infiltration of surface water into the aquifer. Natural site material was used to fill the well bore of deeper wells from the Bentonite seal to a depth of about 3 ft below ground surface. The well was completed to ground surface with the installation of a metallic manhole and lid set in concrete. A locking well cap and lock were installed in each monitoring well to prevent unauthorized access and a metal identification tag was affixed in the manhole.

3.2. MONITORING WELL LOCATIONS

Monitoring wells were installed in four cross sections at the Sampson County site to define the vertical and horizontal distribution of contaminants (Figure 3-1): line A, at the source; line B, 137 ft downgradient; line C, 290 ft downgradient; and line D, 580 ft downgradient. The most downgradient line of wells was positioned to represent the "end" of the BTEX plume as of May 1993 and yet was close enough to the source to provide reasonably accurate analytical results. Monitoring well clusters were advanced along each cross section at approximately 50-ft intervals until the section endpoint wells were found to be free of contamination. Because of

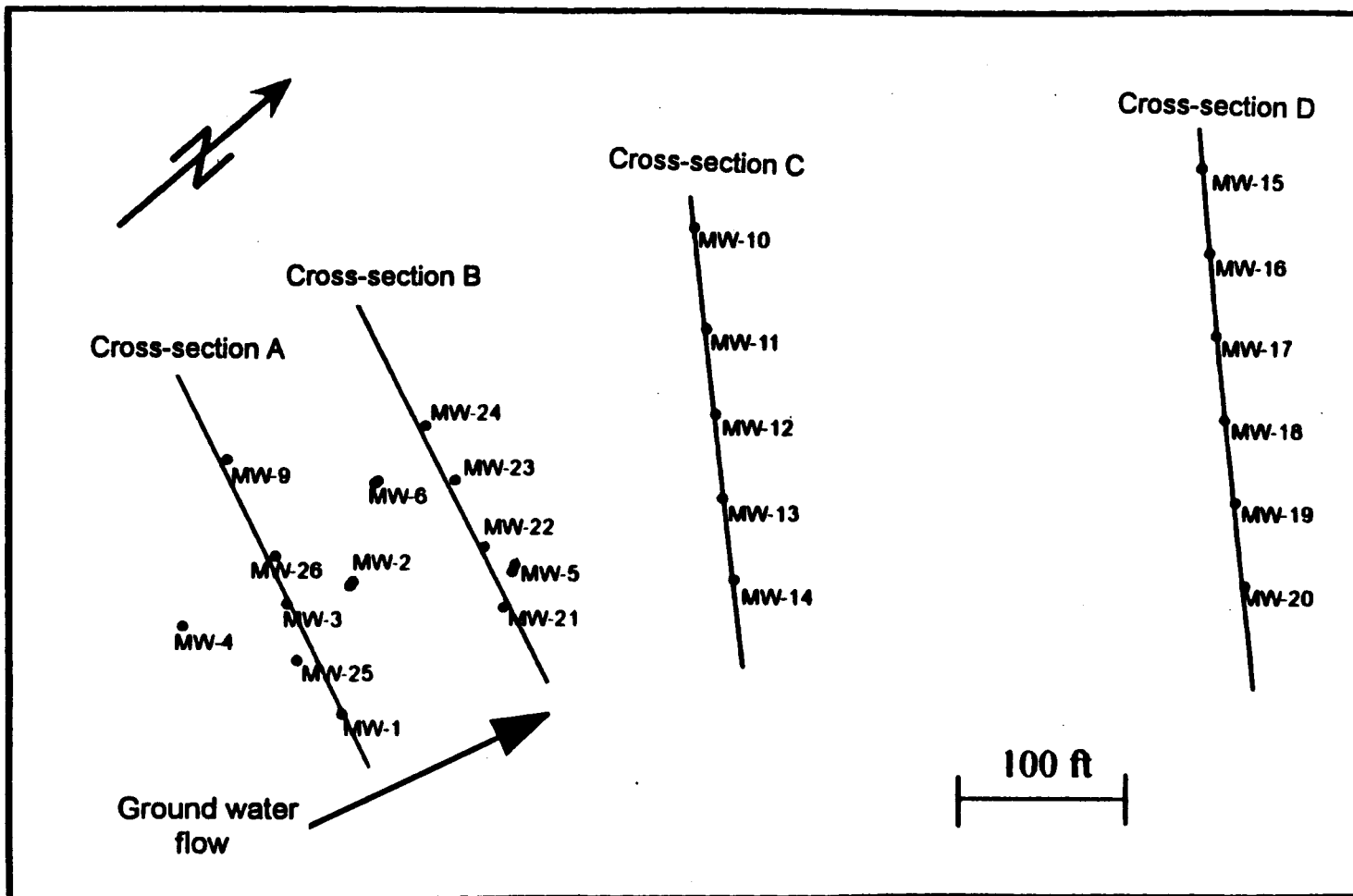


Figure 3-1. Monitoring Well Location Map.

seasonal shifts in the groundwater flow direction, low levels of BTEX and MTBE have occasionally been detected in the outermost wells. At most locations, a well cluster consisting of three 5-foot well screens was installed to define the vertical distribution of contaminants through the full saturated thickness of the aquifer. One monitoring well screen (shallow or "s") was installed across the water table interface, and a second well screen (deep or "d") was installed immediately above the clay-confining layer present at 25 to 30 ft below grade. A third well screen (middle or "m") was installed midway between the upper and lower well screens. A slight overlapping of well screens occurs at some of the well clusters. Monitoring wells were constructed of 2.0-in.-diam. PVC well casing with a 5.0-ft-long, 0.01-in. slotted PVC screen; natural sand pack; Bentonite pellet seal; and flush mount locking cover. A 5-ft screened interval was chosen over discreet sampling points to provide more accurate estimates of vertically averaged concentrations. These vertically averaged concentrations will be used in calculations of the mass flux of contaminants through the aquifer. The wells in line B deviated slightly from the standard cross-sectional arrangement to meet the aesthetic considerations of the property owner. Though some of the original monitoring wells do not lie on plume cross sections, they were sampled for long-term reference. The coordinates and screened intervals for all monitoring wells are provided in Section 4.0 of Appendix A (Borden *et al.*, 1997).

3.3. GROUNDWATER SAMPLING

Groundwater samples were collected from all wells and analyzed for BTEX, MTBE, and indicator parameters 11 times between Spring 1993 and Fall 1995. Several of the upgradient wells were also monitored beginning in June 1992. Groundwater samples were collected and handled according to the protocol described by Barcelona *et al.* (1988) with the following sequence of operations: (1) Well Purging, (2) Sample Collection, (3) Field Blanks, (4) Field Determination, (5) Preservation/Storage, and (6) Transportation.

A dedicated Waterra[®] model D-25 inertial pump attached to a section of high density polyethylene tubing was installed in each monitoring well. Groundwater samples were obtained

by vertically oscillating the tubing, advancing a column of water to the ground surface. During sampling, a short section of new vinyl tubing was attached to the end of the polyethylene tubing to allow for easier sample collection.

Before sampling, the monitoring well head space was purged with purified argon gas to prevent the introduction of oxygen into the samples. At least five well volumes were pumped from the well prior to sample collection. A total of four 40-mL borosilicate vials with Teflon[®]-lined septa and plastic caps were collected from each well. To prevent volatilization of organics, all samples were collected without head space and with caps affixed tightly.

Samples were collected, filtered, labeled, and preserved according to the information shown in Table 3-1. Field samples were stored in large insulated ice chests full of ice and were transported to the NCSU Environmental Engineering Laboratories. In the laboratory, samples were stored in an ignition-safe refrigerator at 4°C and were analyzed within 48 hours of arrival.

Table 3-1. Sample Collection and Preparation Protocol.

Analysis	Container	Label ID	Filter	Preserved
Volatile Organics	40 mL Vial	MW-X GC-1	No	Yes, 0.5 mL of 2.0 N HCl
Organics Back-up	40 mL Vial	MW-X GC-2	No	Yes, 0.5 mL of 2.0 N HCl
Nutrients	40 mL Vial	MW-X SS-NP	Yes 0.45 µm	NO
Metals	40 mL Vial	MW-X SS-HCl	Yes 0.45 µm	Yes, 0.5 mL of 2.0 N HCl

Groundwater testing was conducted in the field for DO, dissolved CO₂, pH, Eh, and temperature. Groundwater temperature and DO were measured using an Orion[®] model 840 Dissolved Oxygen Meter. The DO meter probe was introduced into the well in the middle of the screened interval. Keeping the probe stationary in a sample results in DO readings that continuously decrease with

time. Therefore, the probe was slowly oscillated up and down over a total distance of about 1 ft until readings stabilized. Sample pH and Eh were measured by identical Orion® model 920 ISE meters using an Orion® pH triode and a Corning® platinum redox electrode model 96-78-00. Field CO₂ measurement was carried out using a Hach® Method 8205 digital titrator.

3.4. LABORATORY ANALYTICAL METHODS

NCSU performed laboratory analysis of organic compounds (BTEX and MTBE) using a Tekmar® Purge-and-Trap Model LSC 2000 with a Perkin-Elmer® Model 9000 Auto System Gas Chromatograph fitted with a 75m DB®-624 Megabore capillary column.

NCSU Soil Science Department Analytical Service Laboratory analyzed samples collected for inorganic nutrients, anions, and metals. Sample analysis for Cl⁻, Br⁻, and SO₄²⁻ was conducted on a Dionex® Ion Chromatograph. A Perkin-Elmer Plasma II Ion Coupled Argon Emission Spectrometer (ICP-AES) was used for determination of soluble concentrations of sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), aluminum (Al), nickel (Ni), copper (Cu), manganese (Mn), zinc (Zn), and silica (Si). Nitrogen compound analysis was performed using a LACHAT® auto analyzer and a spectrophotometric method was used for phosphorus analysis. Starting with the October 1994 sampling event, several of the Soil Science Department analyses were discontinued because their results had shown little variation with time. From this period forward, the Soil Science Department analyzed NO₃⁻, NO₂⁻, total organic carbon, and Cl⁻.

Chapter 4

SPATIAL DISTRIBUTION OF BTEX AND INDICATOR PARAMETERS

4.1. GEOCHEMICAL INDICATOR PARAMETERS

Background DO concentrations at this site ranged from 7 to 8 mg/L. Background nitrate concentrations in the aquifer varied from 7 to 17 mg/L $\text{NO}_3\text{-N}$ because of extensive fertilization of fields surrounding the site. Dissolved iron was low in most wells (<0.1 to 0.4 mg/L). However, 1 to 2 mg/L of dissolved iron were detected in the more highly contaminated wells (MW-3, MW-23, and MW-26). The presence of dissolved iron in a few contaminated wells at low levels indicates that while some iron reduction may have occurred in this aquifer, it was not a major electron acceptor. Dissolved sulfate concentrations ranged from less than <0.5 to 8 mg/L throughout the aquifer and did not appear to follow any consistent pattern. Methane was never observed above the analytical detection limit of 0.01 mg/L in any well. The oxidation-reduction potential ranged from +200 to +450 mV. While redox potentials were often lower in the most contaminated wells, they were always greater than +200 mV indicating oxidizing conditions in all wells. These results indicate that the presence of oxygen and nitrate buffers the oxidation-reduction potential in this aquifer. While minor amounts of iron reduction may occur, the major electron acceptors available for hydrocarbon biodegradation in this aquifer are oxygen and nitrate.

The temperature of the aquifer ranged from 15 to 21°C. Dissolved ammonia (NH_4 as N) was below the detection limits of 0.5 mg/L in most wells. Low levels of ammonia (0.5 to 2.0 mg/L as N) were often detected in the source area (MW-3), possibly due to use of ammonia-based fertilizers in a nearby shed or assimilatory nitrate reduction. Dissolved phosphate ranged from 13 to 339 $\mu\text{g/L}$ as P across the site. These phosphate concentrations are low; however, they are comparable to background phosphate levels observed by Swindoll *et al.* (1988) and Armstrong *et al.* (1991). In both of these studies, increases in phosphate at some locations resulted in an increase in the rate of biodegradation and/or reduced the lag period, while in other samples from the same or adjoining locations, phosphate addition had little or no effect.

The average pH was 4.3 (sd = 0.3) and alkalinity ranged from 12 to 30 mg/L as CaCO₃. The low pH and acid neutralization capacity indicate that the aquifer has a weak buffering capacity. These pH values are low but should be adequate for aerobic biodegradation. Denitrifiers are more sensitive to pH and may be inhibited by the low pH found in the aquifer. Denitrification rates are usually optimal at a pH between 7 and 9 and may drop off rapidly below pH 6 (Delwiche and Bryan, 1976). Studies have shown that although denitrification can occur at pH values as low as 4, the rate of denitrification is reduced (Parkin *et al.*, 1985; Tiedje, 1988). The low pH levels at this site may be limiting BTEX biodegradation in the presence of excess nitrate.

High concentrations of total dissolved solids, sodium, and chloride were regularly observed in selected wells in the aquifer. These elevated concentrations are due to NaCl released into the aquifer from a salt house that was formerly located adjoining MW-25 (50 to 75 ft from source). A distinct NaCl plume emanates from this area and migrates downgradient following the same general pattern as the MTBE and BTEX plumes. No significant variations were observed in the parameters Al, Br, Ca, Cd, Cu, Mg, Mn, Ni, Si, and Zn.

4.2. VARIATION OF BTEX WITH TIME

Groundwater samples have been collected from the complete well network and analyzed for dissolved BTEX and MTBE 11 times since May 1993. Several of the upgradient wells were also monitored for BTEX starting in June 1992. Concentration versus time plots were evaluated to determine if there were significant trends in contaminant concentration versus time. The time axis on these plots is referenced to January 1, 1992, as day 1; however, monitoring by NCSU did not begin until day 170.

In the area immediately adjoining the former USTs, total BTEX concentrations vary from 10–20 mg/L in MW-3m to 60–80 mg/L in MW-26m (Figure 4-1A). The lower concentrations in MW-3m are likely due to the greater amount of contaminated soil removed in this area. There were no detectable trends in BTEX concentration with time in either well or detectable correlation with water table elevation.

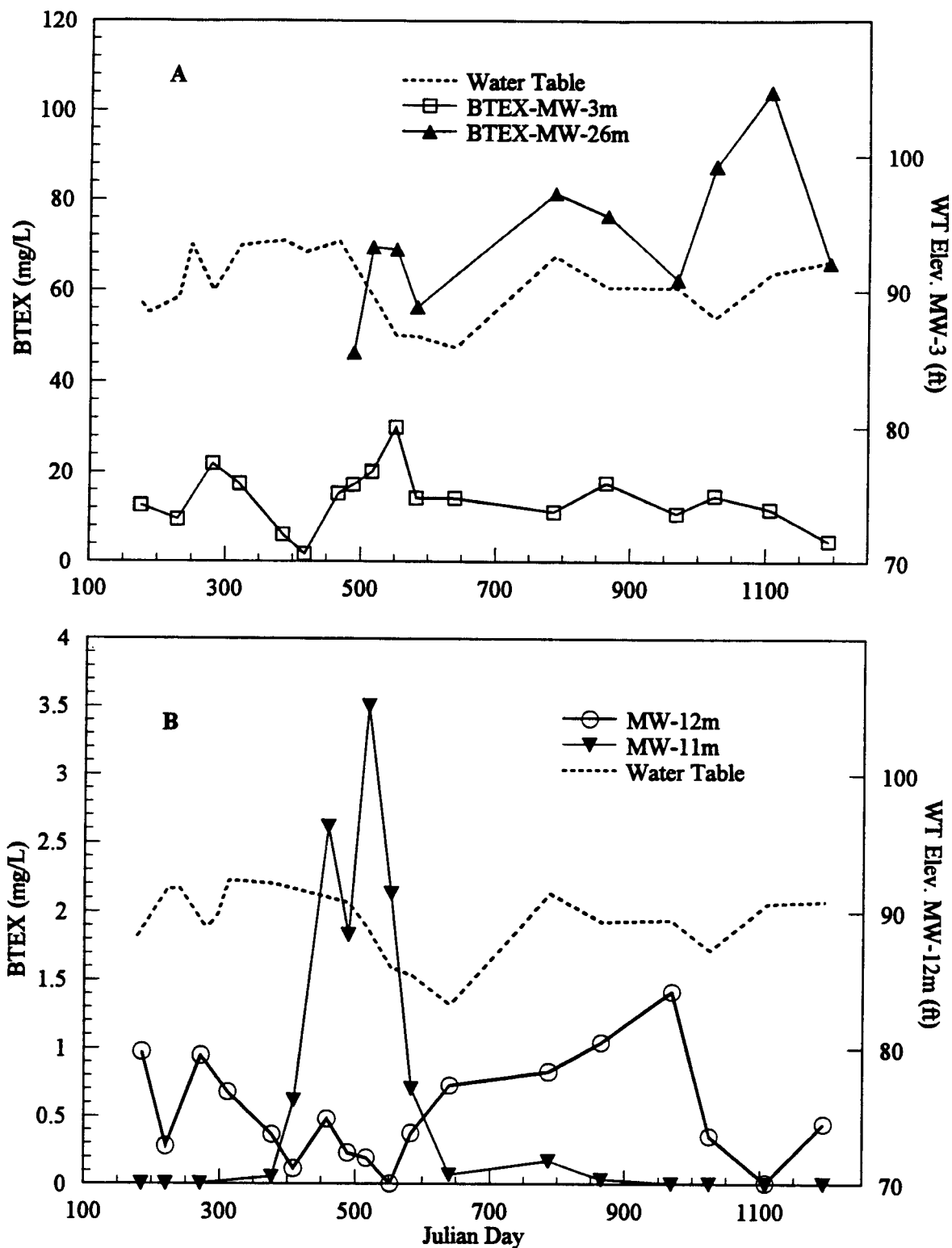


Figure 4-1. Variation in Total BTEX Concentration with Time and Water Table Elevation in (A) MW-3s and in (B) MW-11m and MW-12m (Julian Day 0 = 1/1/92).

At well line C, the center of the plume shifts in response to changes in groundwater flow direction. During the period from day 250 to 500, BTEX concentrations decreased in MW-12m and increased in MW-11m (Figure 4-1B). During this same period, the water table was high and groundwater flow was in a more northerly direction. After day 500, the water table fell and the flow shifted to a more easterly direction that resulted in higher BTEX concentrations in MW-12m and lower concentrations in MW-11m. Here also, we have not observed any long-term trends in contaminant concentrations.

MTBE and BTEX concentrations are plotted versus time in Figure 4-2 for MW-17m, one of the most contaminated wells in line D. When these wells were installed in the Spring of 1993 (500 days), line D was positioned downgradient of the leading edge of the BTEX plume but within the MTBE plume. Shortly after installation of these wells, benzene, o-xylene, and MTBE concentrations began to increase indicating that these compounds were continuing to migrate downgradient. However, by day 700, benzene, o-xylene, and MTBE stabilized at pseudo-steady-state concentrations of ~100, ~40, and ~250 µg/L, respectively. After day 800, toluene and m-, p-xylene increased slightly and then declined, while ethylbenzene remained at or below the analytical detection limit (< 1 µg/L). The more rapid breakthrough of benzene does not appear to be strictly due to hydrophobic sorption since o-xylene followed a nearly identical pattern. In contrast, ethylbenzene and m-, p-xylene never broke through at significant concentrations. If hydrophobic sorption was the only attenuation mechanism, ethylbenzene; o-xylene; and m-, p-xylene should migrate at similar rates since they have similar aqueous solubilities and octanol-water partition coefficients. The initial increase and subsequent decline in toluene and m-, p-xylene may be due to gradual microbial adaptation to these compounds and subsequent biodegradation.

4.3. HORIZONTAL AND VERTICAL DISTRIBUTION OF CHLORIDE, OXYGEN, NITRATE, AND INORGANIC CARBON

Plan views and vertical cross sections of the chloride, oxygen, nitrate and total carbon dioxide plumes in April 1995 are shown in Figure 4-3 to 4-6. Dots indicate the location of the monitoring well clusters. In the cross sections, crosses indicate the center of the monitoring well screens.

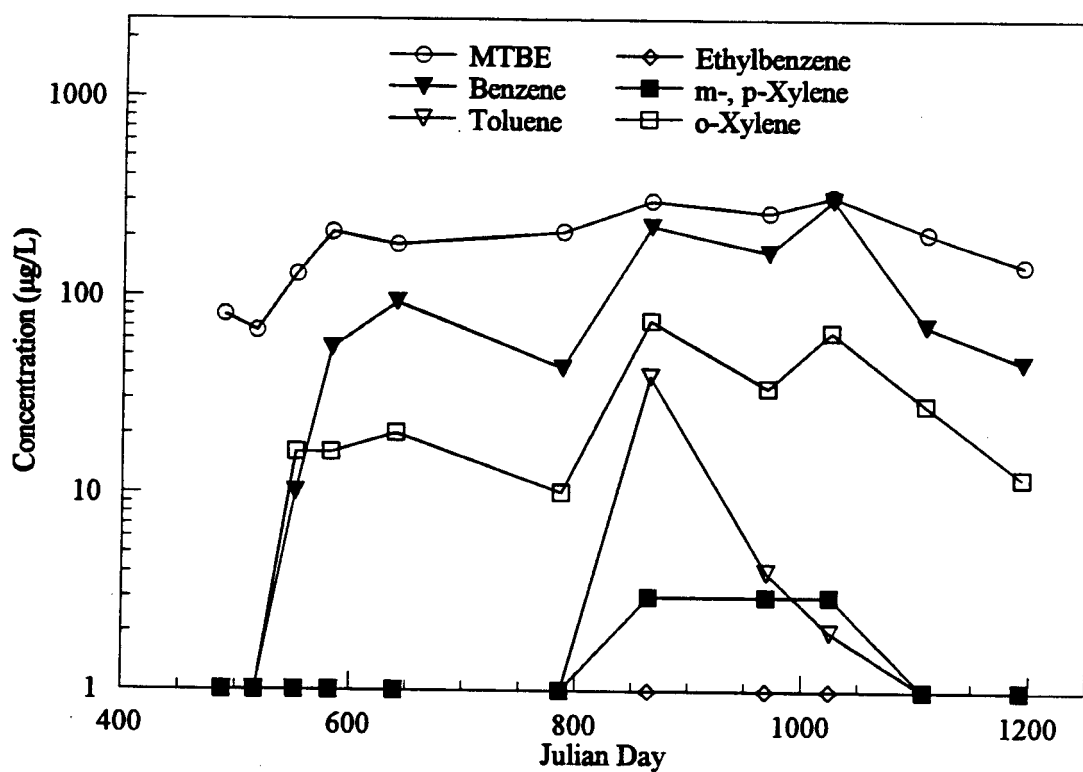


Figure 4-2. Variation in MTBE and BTEX Components with Time in MW-17m (Julian Day 0 = 1/1/92).

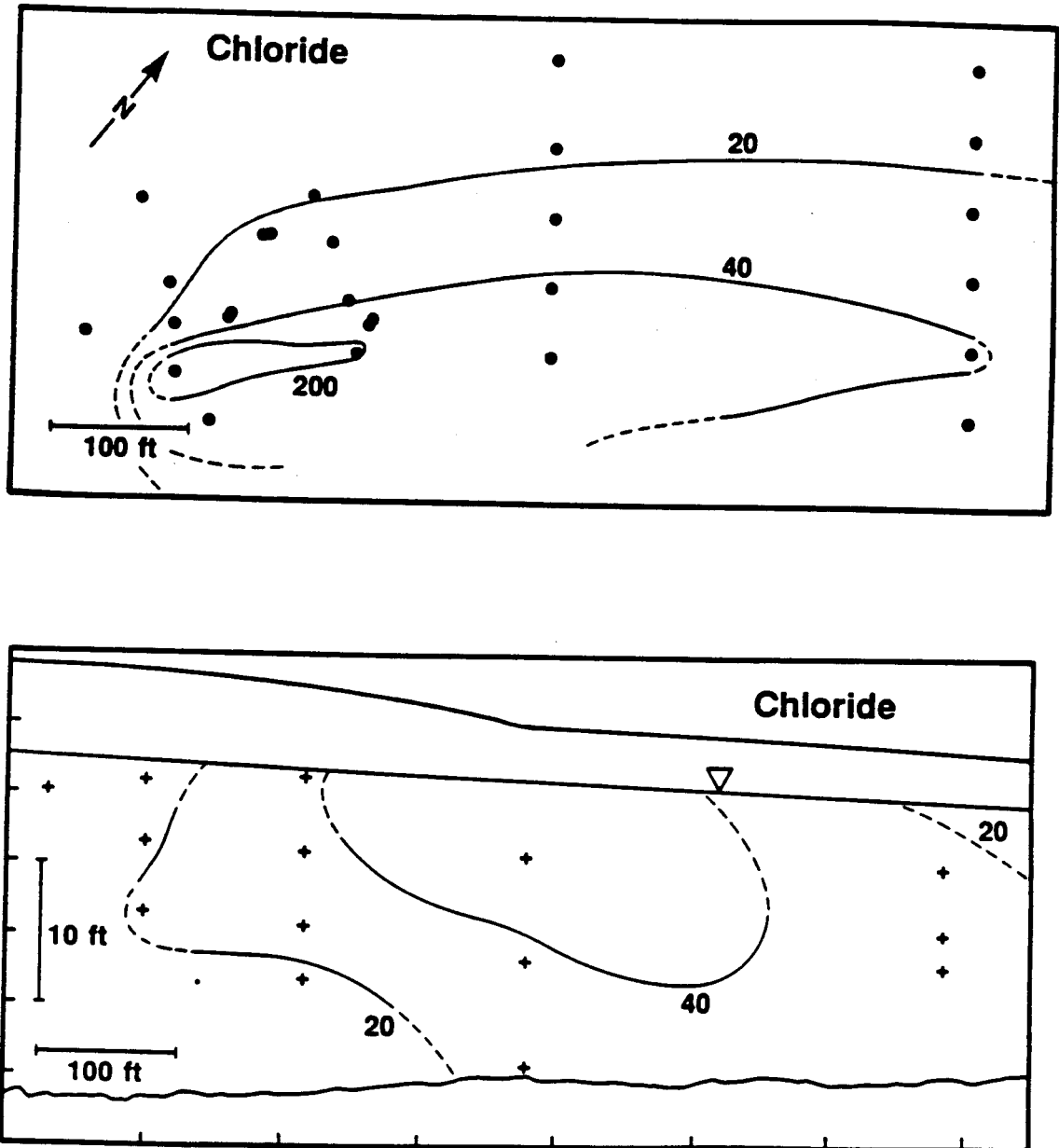


Figure 4-3. April 1, 1995, Chloride Concentration Distribution (mg/L): Plan and Profile Views.

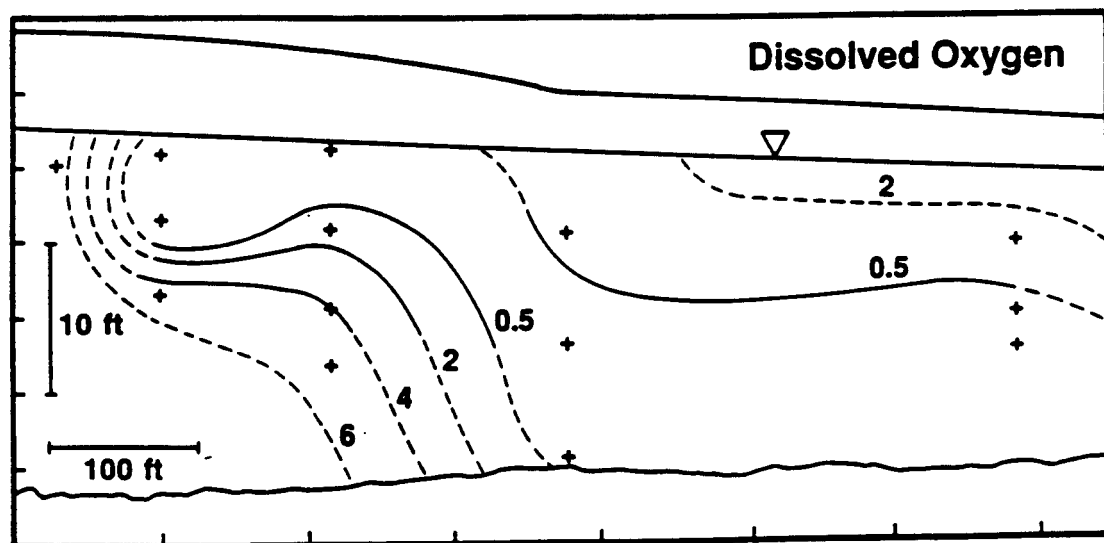
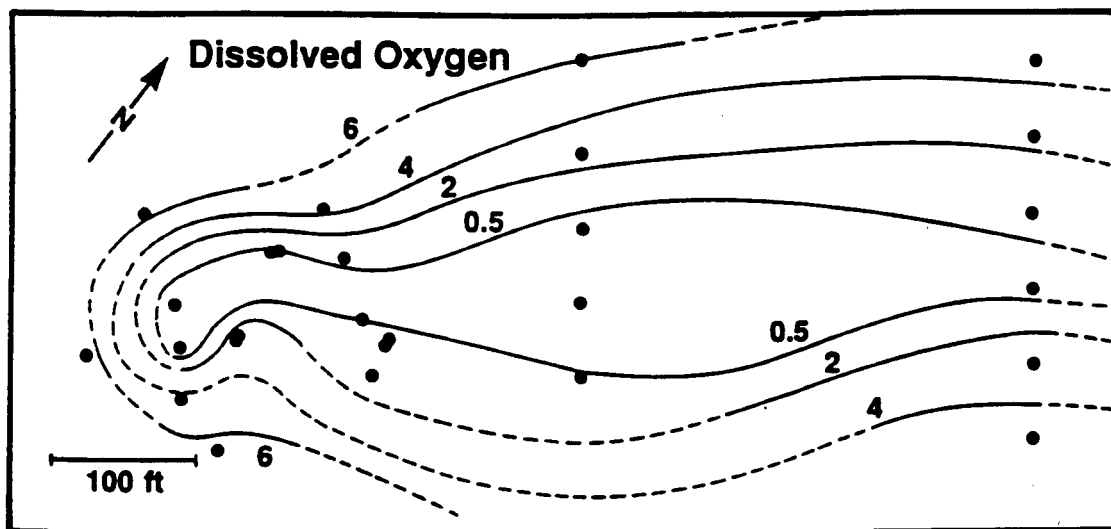


Figure 4-4. April 1, 1995, Dissolved Oxygen Concentration Distribution (mg/L): Plan and Profile Views.

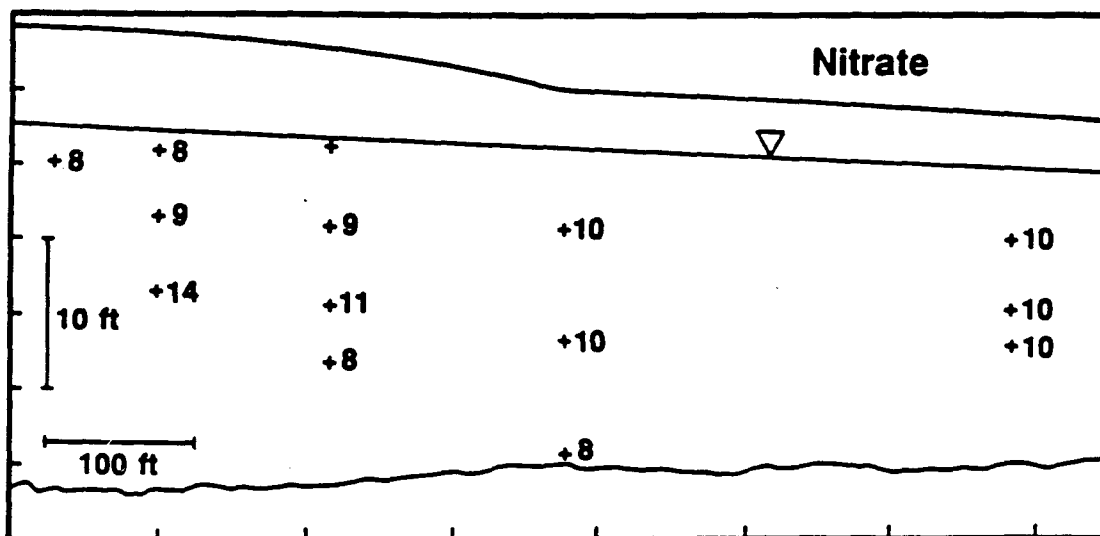
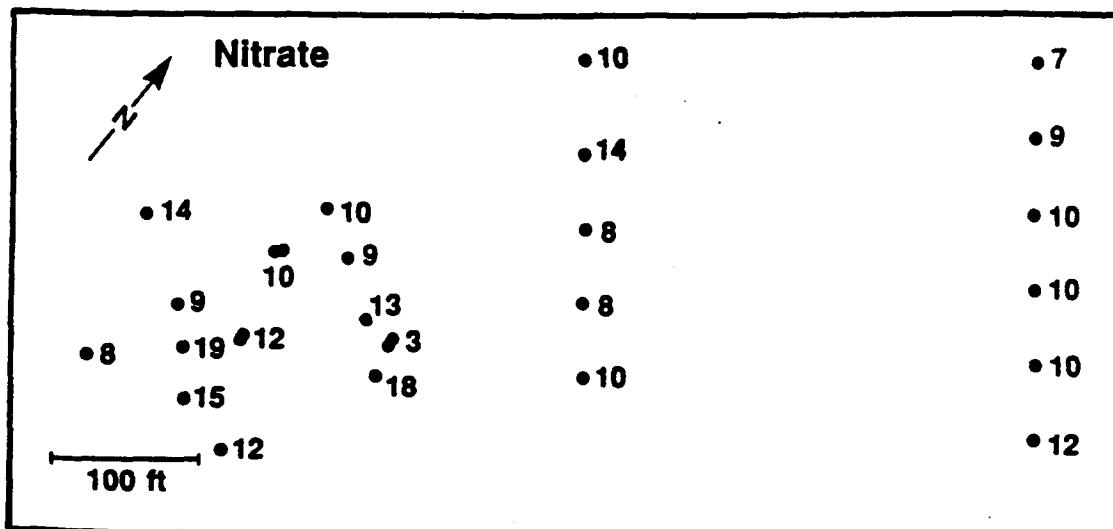


Figure 4-5. April 1, 1995, Nitrate Concentration Distribution (mg/L): Plan and Profile Views.

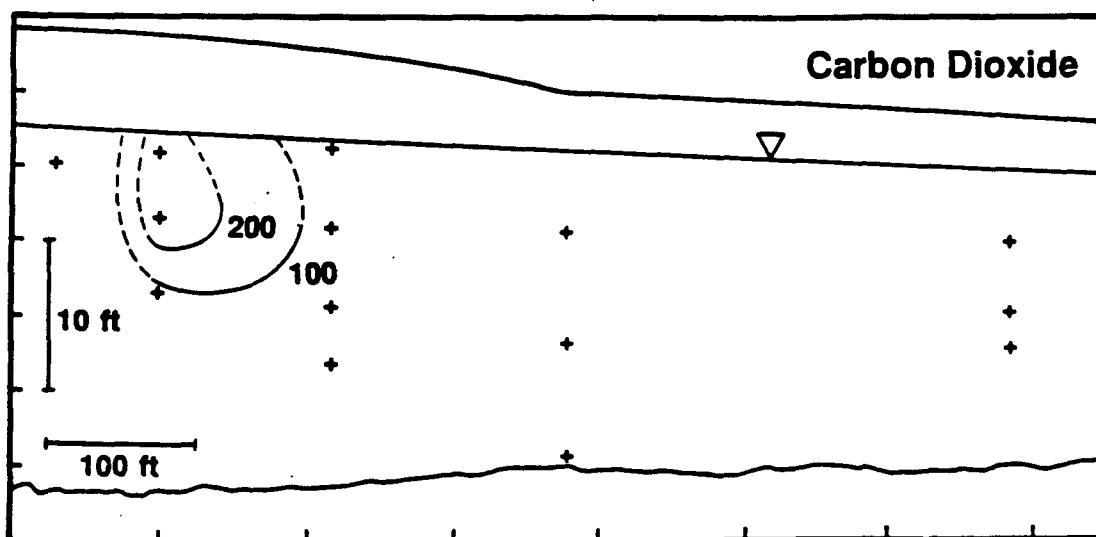
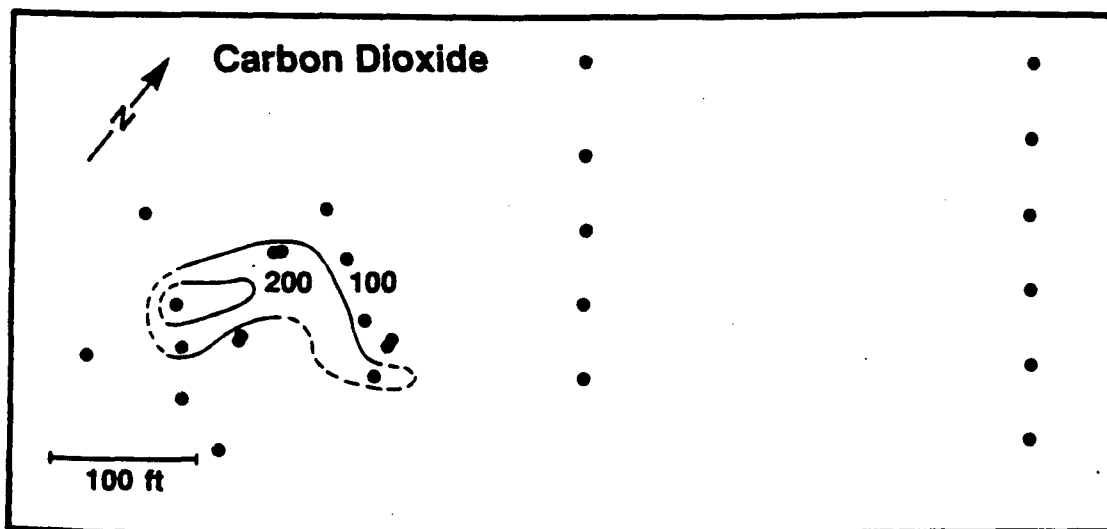


Figure 4-6. April 1, 1995, Carbon Dioxide Concentration Distribution (mg/L): Plan and Profile Views.

The plan views were plotted for the vertical interval of the aquifer with the highest MTBE and BTEX concentrations (line B-B' in Figure 2-2). The cross sections were drawn along the approximate MTBE/BTEX plume centerline as of April 1995 (line A-A' in Figure 2-1). Because of this procedure, the cross section does not follow the chloride plume centerline. The contours were drawn by linearly interpolating between the closest data points.

The chloride plume emanates from a former salt house located near MW-25 and migrates to the northeast following the general groundwater flow direction (Figure 4-3). Because the chloride plume originates to the east of the BTEX plume, it was not entirely intercepted by the network of monitoring wells. The large spread of the chloride plume is believed to result from changes in the groundwater flow direction. At well line C, the plume bends slightly to the east. A shallow (3-ft-deep) drainage tile is located approximately 100 ft northwest of the northern most well in this line (MW-10). When the water table is high, this drain pulls the plume to the northwest. When the water table is below the drain elevation, the plume follows the regional groundwater flow toward a small stream located 1200 ft to the northeast of the 580-ft line of wells.

DO concentrations outside the BTEX plume range from 7 to 8 mg/L, while in the center of the plume, DO concentrations are below the field detection limit of 0.5 mg/L (Figure 4-4). As in previous work, when DO concentrations exceeded 1.0 mg/L, dissolved hydrocarbon concentrations were close to the analytical detection limit (Chiang *et al.*, 1989; Borden *et al.*, 1986, 1995). However, at this site, low concentrations of dissolved hydrocarbons were sometimes present (< 100 µg/L benzene) when DO concentrations were low (0.5 to 1.0 mg/L).

Nitrate concentrations varied (7 to 19 mg/L NO₃-N) throughout the site, and there was no evidence of a zone of depressed nitrate concentrations similar to the DO distribution (Figure 4-5). While low nitrate concentrations did occasionally coincide with high BTEX levels, this pattern was not consistent throughout the site or over time. The high background nitrate concentrations are due to extensive fertilization of the farmland surrounding the site. The absence of a detectable depression in NO₃-N associated with the dissolved BTEX plume is believed to be due to spatial variability in groundwater recharge and fertilizer application rates. Given the high NO₃-N

concentrations in the aquifer, nitrate availability should not limit BTEX biodegradation via denitrification.

A plume of elevated total carbon dioxide (CO₂) was present in the aquifer (Figure 4-6) and coincides with the BTEX plume. CO₂ is produced as a result of organic carbon biodegradation, demonstrating that hydrocarbon biodegradation is occurring. Background inorganic carbon concentrations ranged from 25 to 50 mg/L as CO₂. CO₂ concentrations were highest at MW-26 (300 mg/L) and decreased gradually from the source. At the downgradient line of wells, CO₂ concentrations were highest in wells with the highest MTBE and BTEX concentrations.

4.4. HORIZONTAL AND VERTICAL DISTRIBUTION OF MTBE AND BTEX

The horizontal and vertical distributions of MTBE and BTEX components are shown in Figures 4-7 to 4-12. Average contaminant concentrations in the most contaminated wells in each line are listed in Table 4-1 for the 1994–95 monitoring period. Data from 1993 were not included in these averages to eliminate the effects of the gradual breakthrough of contaminants in line D. Concentrations of all contaminants are highest in MW-26m and decrease steadily with distance from the source. MW-26m is located immediately to the northwest of the former USTs, and a sheen of gasoline has occasionally been observed on water samples collected from this well. Toluene and ethylbenzene decline most rapidly with distance from the source followed by m-, p-xylene and then o-xylene, benzene, and MTBE. During transport from line A to C, the average peak concentration of toluene; ethylbenzene; and m-, p-xylene decreased by more than 99%; o-xylene, benzene, and MTBE decreased by 97 to 98%.

The o-xylene, benzene, and MTBE plumes all have the same general shape and they flow to the northeast. The width of the MTBE plume is similar to the chloride plume, but the o-xylene and benzene plumes are somewhat narrower than the chloride plume. The narrower plume width is believed to be due to aerobic biodegradation at the plume fringes. The vertical cross sections for o-xylene, benzene, and MTBE all have the same general appearance. The center of each plume sinks gradually with distance. This sinking is believed to be due to recharge of clean oxygenated water on top of the contaminant plumes. While the general appearance of the MTBE and benzene

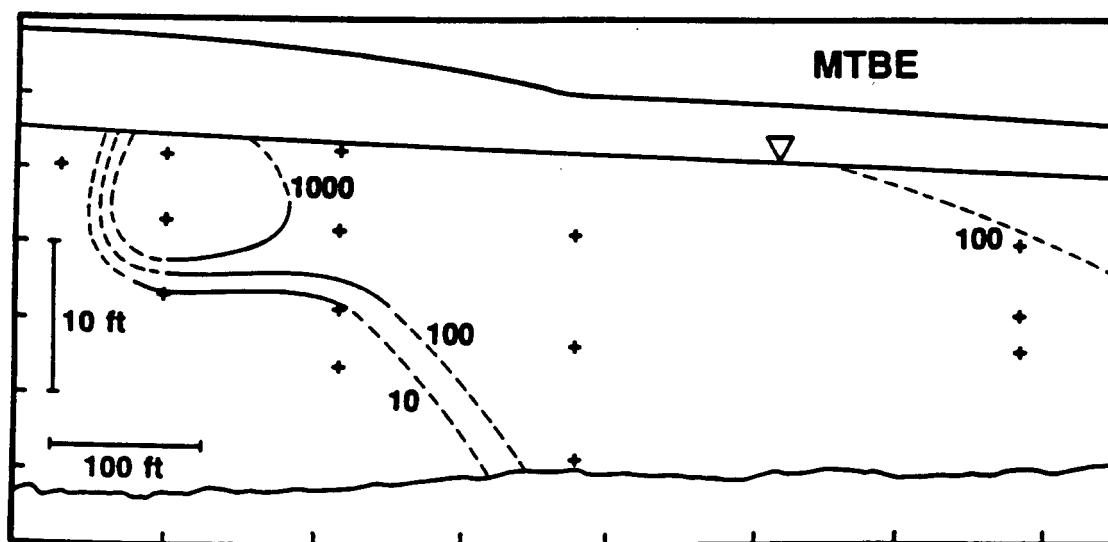
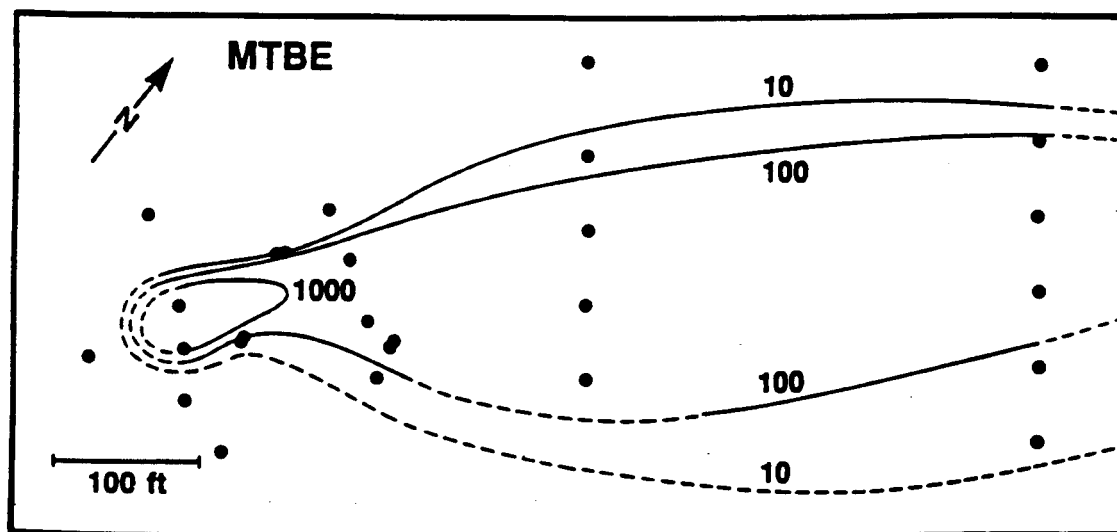


Figure 4-7. April 1, 1995, MTBE Concentration Distribution ($\mu\text{g/L}$): Plan and Profile Views.

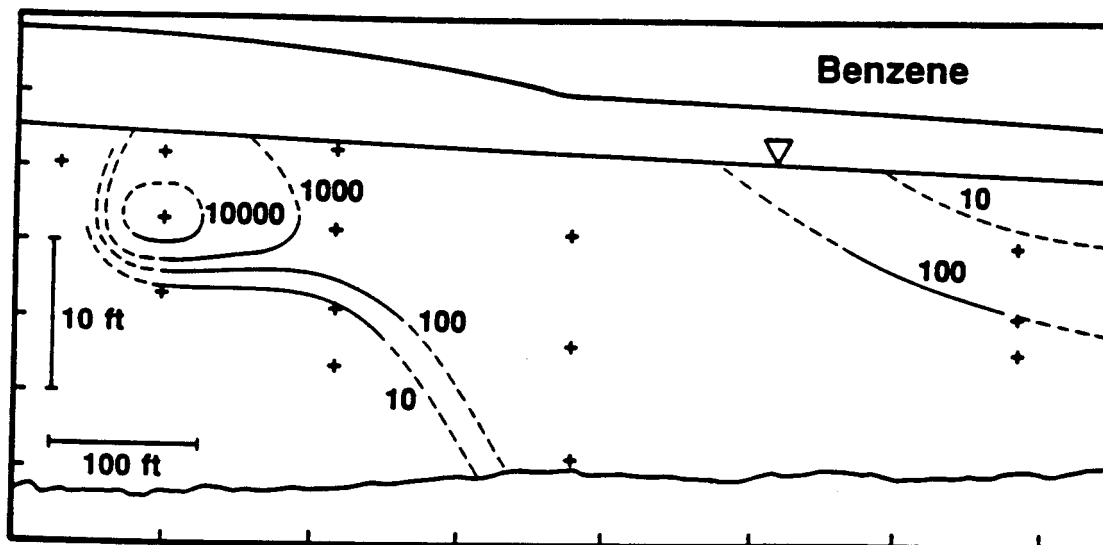
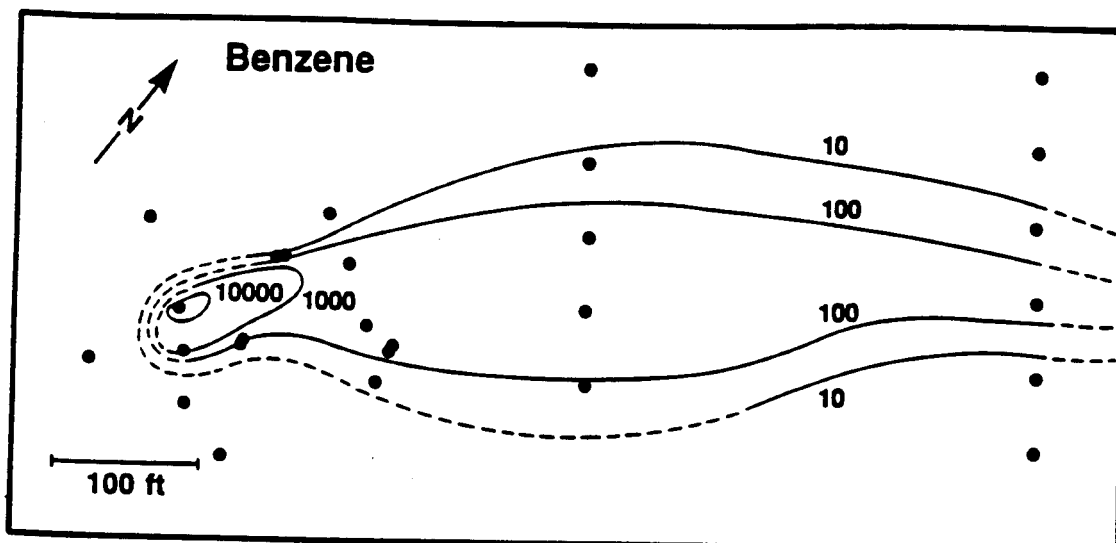


Figure 4-8. April 1, 1995, Benzene Concentration Distribution ($\mu\text{g/L}$): Plan and Profile Views.