

Transport and Fate of Dissolved Methanol, Methyl-Tertiary-Butyl-Ether, and Monoaromatic Hydrocarbons in a Shallow Sand Aquifer

HEALTH AND ENVIRONMENTAL SCIENCES
API PUBLICATION NUMBER 4601
APRIL 1994



American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005



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Health and Environmental Sciences Department

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ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

API STAFF CONTACT

Roger Claff, Health and Environmental Sciences Department

MEMBERS OF THE SOIL AND GROUNDWATER TECHNICAL TASK FORCE

Dorothy Keech, Chevron Oil Field Research Company

Victor Kremesec, Amoco Corporation

Al Liquori, Exxon Research and Engineering Company

Eugene Mancini, ARCO

William Rixey, Shell Development Company

Ed Sudicky, Barbara Butler and Colin Mayfield offered useful advice and support. Karen Berry-Spark and Lloyd Lemon designed the field experiment and carried it through the third sample event. L. Lemon continued to assist throughout the field experiment and data analysis. France Beaudet, Jeff Barbaro, Anika Bedard, Doris Dumas, Isabelle Derome, Rick Devlin, Paul Drake, Susan Hipkin, Pat McGuinness, Mette Poulsen and Katherine O'Leary assisted with the field sampling. Ralph Dickhout, Shirley Chatten, Paul Drake and Tracy Fowler performed the laboratory analyses. Ken Skene assisted in data analysis and evaluation of the moment analysis method. Canadian Forces Base Borden allowed the work to proceed on their Base.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
EXECUTIVE SUMMARY	ES-1
1. INTRODUCTION	1-1
2. THE BORDEN TEST SITE	2-1
2.1 Geology	2-3
2.2 Hydrogeology	2-3
2.3 Groundwater Geochemistry	2-5
2.4 Subsurface Microbiology	2-6
2.5 Spatial Distribution of Dissolved Oxygen	2-7
3. THE FIELD EXPERIMENT	3-1
3.1 Injection Solutions	3-1
3.2 Injection Well Configuration	3-3
3.3 Solute Injection System	3-5
3.4 Injection of the Solutes	3-6
3.5 Results of Injection Monitoring	3-6
3.6 Multilevel Sampler Array	3-7
3.7 Monitoring Approach	3-8
3.8 Collection and Analysis of Water Samples	3-10
3.9 Quality of the Solute Concentration Data	3-11
4. DATA MANAGEMENT AND ANALYSIS	4-1
4.1 Data Entry and Correction Procedures	4-2
4.2 Evaluation of Plume Capture	4-3
4.3 Depth Integration of Solute Concentrations	4-5
4.4 Projection to a Regular Grid	4-6
4.5 Spatial Moment Estimation	4-6
4.6 Discussion of Sources of Error in Mass Estimation	4-7

TABLE OF CONTENTS (continued)

<u>Section</u>	<u>Page</u>
5. OVERVIEW OF SOLUTE BEHAVIOR	5-1
5.1 Areal Distributions of Solute Mass	5-1
5.2 Vertical Solute Concentration Distributions	5-19
5.3 Aquifer Layering and Solute Distribution	5-25
5.4 Summary and Discussion of Observations	5-27
6. TRANSPORT OF THE SOLUTES	6-1
6.1 Horizontal Center of Mass Trajectories	6-1
6.2 Velocities of Plume Movement	6-3
6.3 Field Retardation	6-7
6.4 Laboratory Sorption Experiments	6-9
6.5 Spatial Variance and Dispersion	6-11
6.6 Summary and Discussion of Solute Transport Findings	6-14
7. ESTIMATES OF SOLUTE MASS	7-1
7.1 Estimates of Injected Mass	7-1
7.2 Mass Estimates for Sample Rounds	7-2
7.3 Rates of Mass Loss	7-16
7.4 Discussion of Mass Loss Findings	7-18
8. LABORATORY BIOTRANSFORMATION STUDY	8-1
8.1 Experimental Approach and Design	8-1
8.2 Interpretation of Microcosm Data	8-3
8.3 Biotransformation of the Monoaromatics	8-4
8.4 Persistence and Impact of MTBE	8-6
8.5 Persistence and Impact of Methanol	8-7
9. FIELD BIOTRANSFORMATION	9-1
9.1 Oxygen and BTEX Persistence	9-1
9.2 Oxygen and Methanol Persistence	9-7
9.3 Impact of Methanol on BTEX Persistence	9-15
9.4 Comments on Field Biotransformation Findings	9-17



TABLE OF CONTENTS (continued)

<u>Section</u>	<u>Page</u>
10. CONCLUSIONS AND IMPLICATIONS	10-1
10.1 General Solute Flow	10-1
10.2 Transport of the Organic Solutes	10-1
10.3 Biotransformation of the Monoaromatics	10-2
10.4 Fate and Impact of MTBE	10-3
10.5 Fate and Impact of Methanol	10-3
10.6 Extension of Findings to Other Hydrogeological Settings	10-4
REFERENCES	R-1

LIST OF APPENDICES

A.	The Field Injection	A-1
B.	The Monitoring Network	B-1
C.	Sample Collection Procedures	C-1
D.	Laboratory Analytical Procedures	D-1
E.	Surface II Parameters	E-1
F.	Locations of Plume Cross Sections	F-1
G.	Transport and Fate Data	G-1
H.	Laboratory Biotransformation Studies	Under Separate Cover

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1-1. Hydrophobicity Parameters for the Solutes at 25°C	1-3
2-1. Characteristics of the Borden Aquifer	2-4
2-2. Chemistry of the Aerobic Zone of the Borden Aquifer	2-6
3-1. Average Solute Concentrations in the Injection Solutions (mg/L)	3-7
3-2. Summary of Sampling Rounds	3-9
6-1. Horizontal Velocities of the Chloride Plumes (cm/day)	6-6
6-2. Range of Average Field Retardation Factors Calculated for the Organic Solutes	6-8
6-3. Average Retardation Factors for the Organic Solutes from Day 6 to 106	6-9
6-4. Retardation Factors Calculated from K_{ds}	6-10
6-5. Dispersivities of Freyberg (1986) and this Study	6-13
7-1. Estimates of Injected Mass (grams)	7-1
7-2. Estimates of Total Chloride Mass for each Sample Time (kg)	7-3
7-3. Estimates of Total Oxygenate Mass for Each Sample Time (kg)	7-6
7-4. Estimates of Total Mass for BTEX at each Sample Time (grams)	7-9
7-5. First Order Mass Loss Rates (day^{-1}) Calculated for Day 6 through Day 476	7-17
9-1. Comparison of Initial Conditions for the Natural Gradient Tests of Berry-Spark <i>et al.</i> (1987) and this Study	9-5
9-2. Comparison of First Order Mass Loss Rates (day^{-1})	9-7

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2-1. (a) Map of southern Ontario and the Great Lakes showing the location of CFB Borden; (b) Plan view of the test site in the Borden sand quarry showing the 1979 boundaries of the landfill leachate plume; (c) Site cross section showing the injection zone (after Mackay <i>et al.</i> , 1986)	2-2
2-2. Longitudinal profiles of background dissolved oxygen distribution for the three injection zones.	2-8
2-3. Transverse profile of background dissolved oxygen distribution at the three injection zones.	2-9
3-1. Plan view of the final array of multilevel samplers and locations of the injection wells.	3-4
5-1. Contour plots of depth integrated chloride data for the first, third, fourth and sixth sample rounds	5-3
5-2. Contour plots of depth integrated MTBE and methanol data for the first, third, fourth and sixth sample rounds	5-6
5-3. Contour plots of depth integrated benzene data for the first, third, fourth and sixth sample rounds	5-9
5-4. Contour plots of depth integrated toluene data for the first, third, fourth and sixth sample rounds	5-12
5-5. Contour plots of depth integrated p-xylene data for the first, third, fourth and sixth sample rounds	5-15
5-6. Contour plots of depth integrated m-xylene data for the first, third, fourth and sixth sample rounds	5-17
5-7. Profiles of chloride concentration along the centerline of the 85% methanol plume on Day 106 and Day 476	5-20
5-8. Profiles of benzene, chloride, and methanol concentration along the centerline of the 85% methanol plume on Day 317	5-22
5-9. Profiles of toluene concentration along the centerline of the 85% methanol plume on Day 106 and Day 398	5-23
5-10. Profiles of p-xylene concentration along the centerline of the 85% methanol plume on Day 398 and Day 476	5-24
5-11. Profiles of hydraulic conductivity (after Patrick, 1986) and chloride, benzene, m-xylene, and dissolved oxygen concentration with depth at sampler #4A-N1	5-26

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
6-1. Center of mass trajectories for the chloride, toluene, and p-xylene plumes	6-2
6-2. Plot of distance traveled vs. time for solutes in the 100% PS-6 gasoline control plume	6-4
6-3. Plots of distance traveled vs. time for solutes in the 10% MTBE and 85% methanol plumes	6-5
6-4. Longitudinal and horizontal transverse variance for chloride in the 100% PS-6 gasoline control and the 85% methanol cases.	6-12
7-1. Plots of mass vs. time for chloride in the 100% PS-6 gasoline control plume.	7-3
7-2. Plots of mass vs. time for chloride in the 10% MTBE and 85% methanol plumes.	7-5
7-3. Plots of mass vs. time for MTBE and methanol.	7-7
7-4. Plots of benzene mass vs. time for the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control	7-10
7-5. Plots of ethylbenzene mass vs. time for the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control	7-11
7-6. Plots of p-xylene mass vs. time for the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control	7-12
7-7. Plots of o-xylene mass vs. time for the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control	7-13
7-8. Plots of toluene mass vs. time for the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control	7-14
7-9. Plots of m-xylene mass vs. time for the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control	7-15
8-1. Conceptual illustration of relative concentration vs. time for benzene, toluene, and m-xylene in microcosms containing Borden aquifer material and groundwater contacted by 100% PS-6 gasoline	8-5
8-2. Persistence of MTBE in unlimited oxygen microcosms	8-7
8-3. Persistence of methanol in unlimited oxygen microcosms	8-8



LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
9-1. BTEX and dissolved oxygen distributions in a transverse cross section through the three plumes at the fourth sample round	9-3
9-2. Cumulative oxygen entry into the methanol plume	9-9
9-3. Dissolved oxygen along the plume centerline: Day 106	9-11
9-4. Dissolved oxygen along the plume centerline: Day 317	9-12
9-5. Methanol distributions along the plume centerline on Day 6 and Day 106	9-14



EXECUTIVE SUMMARY

This report presents the results of a field investigation of the fate and transport of two gasoline additives, methanol and methyl tertiary butyl ether (MTBE), in groundwater and the influence of these compounds on the groundwater fate and transport of the gasoline constituents benzene, toluene, ethylbenzene, and xylene (BTEX). Related laboratory experiments which are the subject of a separate report are also summarized.

BACKGROUND

Oxygenates such as MTBE and methanol are added to gasoline to boost octane and/or to reduce air pollution from combustion. Research to date on the effects of gasoline spills to groundwater has focused on the behavior of BTEX, investigating the fate of these compounds in pure form or as constituents of non-oxygenated gasoline. Little is known about the effects of oxygenates on the migration and fate of BTEX in groundwater or the subsurface behavior of the oxygenates themselves.

APPROACH

The field experiment was conducted in a well characterized, unconfined, aerobic sand aquifer at Canadian Forces Base Borden, Ontario, Canada. The study was designed to compare and contrast the behavior of dissolved BTEX and oxygenates from simulated spills of three different types of motor fuels: (1) 100% gasoline, (2) 10% MTBE and 90% gasoline, and (3) 85% methanol and 15% gasoline. A key objective to facilitate data interpretation was to create three dissolved contaminant plumes of similar size that would travel side by side in the same flow system and geochemical environment with minimal lateral overlap. The plumes were created by simultaneously injecting below the water table solutions prepared by contacting extracted groundwater with a standard gasoline (PS-6) and diluting to obtain total dissolved BTEX concentrations of about 18 mg/L. In addition to dissolved BTEX, each solution included sodium chloride (500 mg/L) which acted as a conservative, unreactive tracer. Methanol was added to one of the solutions (7000 mg/L) and MTBE (290 mg/L) was added to a second. The third solution acted as a control.

ES-1

These concentrations were believed to be representative of what could be found at a typical spill site in a plume that has travelled some distance from the source of the release.

Concentrations of the dissolved BTEX, methanol, MTBE, and chloride were monitored in three dimensions using a dense network of multilevel sampling wells. Six sampling events took place over a sixteen month period, and over 8,000 samples were analyzed. To evaluate the average movement of each of the plumes, the total mass, center of mass, and spreading parameters for the plumes were estimated by the statistical technique of spatial moment analysis. A laboratory biotransformation study and a laboratory sorption study aided in interpretation of the field experiment.

RESULTS

The comparative assessment of the fate and transport of both BTEX and oxygenates in the three plumes was accomplished by an evaluation of the relative mobility and persistence of these compounds. Mobility refers to the ease of transport (i.e., the lack of retardation) of the compound in groundwater, using the groundwater velocity as the standard of comparison. Persistence addresses the rate of mass loss due to microbial transformation processes. BTEX and methanol are known to be biodegradable, while MTBE appears to be nondegradable, or perhaps only very slowly degradable.

Mobility

As indicated by the chloride tracers, the three plumes travelled side by side in the aquifer at essentially the groundwater velocity, about 9 cm/day. Calculated longitudinal and horizontal dispersivities were similar for the three cases, indicating that the three plumes encountered the same degree of aquifer heterogeneity along their travel paths. Thus heterogeneity effects did not influence the relative transport of the plumes.

The mobility of methanol and MTBE was similar to chloride, while the monoaromatics; i.e BTEX, were less mobile. The relative mobility of these monoaromatics was reflective

of their relative hydrophobic nature. Benzene was transported at about 90% of the groundwater velocity, toluene at about 75%, and ethylbenzene and the xylene isomers moved at about 67% of the groundwater velocity. Neither MTBE or methanol caused a measurable difference in mobility of the monoaromatics relative to the control case.

Persistence

MTBE was recalcitrant in the aquifer, exhibiting no mass loss over the sixteen month experiment. In contrast, methanol was rapidly degraded after an initial lag period of about 100 days. Less than one percent of the methanol mass remained by the final sampling event. The removal of methanol coincided with an enhanced depletion of oxygen within the boundaries of the 85% methanol/15% gasoline plume relative to the control. Insufficient oxygen was available to account for all of the methanol loss, therefore the methanol is considered to have degraded by first aerobic, then anaerobic, biotransformation.

The monoaromatic hydrocarbons, BTEX, biodegraded in all three plumes. In each of the plumes, the relative rate of biodegradation was: toluene and m-xylene > o- and p-xylene > benzene. This reflects general agreement with other studies that indicate that in BTEX mixtures, toluene and xylenes are preferred substrates for microorganisms as compared to benzene. However, once toluene and xylene concentrations diminish, the rate of benzene degradation increases.

MTBE had no measurable effect on the persistence (biodegradation) of the monoaromatics. Benzene, ethylbenzene, and p-xylene were more persistent in the 85% methanol/15% gasoline plume, indicating that the methanol presence inhibited biotransformation of these compounds. Little effect on toluene and o,m-xylene biodegradation rates was observed. After sixteen months, 50% of the benzene mass remained, whereas in both the control and the 10% MTBE/90% gasoline plume less than 20% of the benzene mass remained after this same time period.

These differences in BTEX mass loss can be explained by analysis of laboratory data from companion studies. Laboratory microcosm experiments showed that at the initial field concentrations (about 7,000 mg/L), methanol can severely constrain metabolism of the monoaromatics, even with unlimited oxygen availability. Based on the laboratory findings and comparison of dissolved oxygen profiles for the methanol and control plumes, the mechanisms of inhibition of the benzene biotransformation in the 85% methanol plume are considered to have been:

- (1) the inhibitory effects of high methanol concentrations on subsurface microbial populations,
- (2) oxygen depletion in the plume core due to methanol biotransformation, and
- (3) preferential microbial utilization of methanol as a substrate (energy source).

CONCLUSIONS

There are many factors that will influence the relative environmental significance of subsurface spills of different types of fuels. The results of this study do indicate the following about the components of the fuel types studied:

- 1) Dissolved BTEX was biodegraded by naturally occurring microorganisms.
- 2) MTBE did not appear to biodegrade to any appreciable extent.
- 3) Methanol was readily biodegradable in groundwater, and is degraded under both aerobic and anaerobic conditions.
- 4) The presence of MTBE had no measurable effect on BTEX biotransformation. However methanol appeared to inhibit the biodegradation of BTEX, either by causing oxygen depletion due to its own biodegradation, by serving as a preferred substrate for microorganisms, or through biochemical effects on microbial cell processes.
- 5) Neither methanol nor MTBE affected the mobility (rate of transport) of dissolved BTEX.
- 6) Both methanol and MTBE traveled at the same rate as the groundwater.

This field study was designed to examine the fate and transport of dissolved BTEX, MTBE and methanol at concentrations estimated to be representative of those that might be found at some distance away from the source area of the release. Dissolved contaminant concentrations at the source of a release will be higher than those studied here. This will be especially true of dissolved methanol concentrations at a subsurface release of a fuel containing 85% methanol and 15% gasoline, because of methanol's complete solubility in water.

Section 1

INTRODUCTION

BACKGROUND

This report presents the findings of a natural gradient tracer test and related laboratory experiments that investigate the subsurface behavior and impacts of methanol and MTBE.

The primary goals of the research were to:

- 1) describe the transport and fate of methanol and MTBE in groundwater; and
- 2) determine the influence of methanol and MTBE on the transport and fate of BTEX in groundwater.

The research was designed to compare and contrast the effects of groundwater contamination by three fuel blends:

- 1) 100% gasoline (control)
- 2) 90% gasoline plus 10% MTBE
- 3) 15% gasoline plus 85% methanol

The study was confined to an evaluation of the dissolved constituents of plumes expected to emanate from spills of these fuels. Behavior of the nonaqueous phase and near-source dissolved phase is being addressed elsewhere (Poulsen, *et al.*, 1991; API/CPPI in review).

Research to date has emphasized the transport and fate of the principal monoaromatic hydrocarbons in gasoline -- benzene, toluene, ethylbenzene, and the xylene isomers (collectively termed BTEX) -- in groundwater. These compounds represent some of gasoline's most water soluble, mobile components. Benzene, a known human carcinogen, is of particular concern (USEPA, 1984) and has a drinking water limit of 5 µg/L in many areas.

Previous studies of the behavior of BTEX in the subsurface have investigated the fate of these compounds in pure form or as derivatives of gasoline with no additives. The research has lead to a broad understanding of BTEX fate, particularly in shallow, aerobic groundwater settings. However, many retail gasoline now contains octane-enhancing additives, typically oxygen-bearing compounds (oxygenates) such as alcohols and ethers.

These additives pose special concerns with respect to groundwater quality because they have higher water solubilities than most other gasoline constituents. They can be expected to occur in extremely high concentrations in groundwater contacted by oxygenate-bearing fuels (API, 1991), and have the potential to influence the subsurface behavior of BTEX. Little is known about the effects of oxygenates on the migration and fate of BTEX in groundwater. The subsurface behavior of the oxygenates themselves has also received little scientific attention. Investigations of the environmental consequences of oxygenate use are needed for informed decision-making on alternative fuel policies.

Two oxygenates, methanol and methyl-tertiary-butyl-ether (MTBE) are the focus of this study. MTBE is used extensively in gasoline in the U.S., principally to meet Clean Air Act requirements, but also as an octane enhancer. Use of methanol as an alternative fuel for vehicles, both in pure form and in an 85% methanol and 15% gasoline blend, has been considered in the United States at both the state and federal level.

Properties of methanol, MTBE and the monoaromatics are listed in Table 1-1. Both oxygenates are highly soluble in water: MTBE has a solubility of 48,000 mg/L and methanol is completely miscible. In contrast, pure-phase BTEX solubilities range from about 200 mg/L (xylenes) to about 1,800 mg/L (benzene). Therefore, the two oxygenates can be expected to occur in high concentrations relative to BTEX at gasoline spill sites. The oxygenates will also be more mobile in the groundwater environment than hydrophobic compounds such as BTEX.

When gasoline is spilled, the nonaqueous phase moves through the soil zone and pools at the water table, leaving behind residual hydrocarbons. Soluble gasoline constituents dissolve into the groundwater and are carried in the direction of flow. The near-source concentrations of the solutes will depend on a variety of factors, in particular their relative proportions in the gasoline blend.

Table 1-1. Hydrophobicity Parameters for the Solutes at 25°C

Solute	Formula	Water Solubility (mg/L)	Log K_{ow}
MTBE	$C_5H_{12}O$	48,000 ⁽⁶⁾	1.20 ⁽⁶⁾
Methanol	CH_4O	miscible	-0.75 ⁽³⁾
Benzene	C_6H_6	1,780 ⁽¹⁾	2.13 ⁽⁴⁾
Toluene	C_7H_8	515 ⁽¹⁾	2.69 ⁽⁴⁾
Ethylbenzene	C_8H_{10}	152 ⁽¹⁾	3.15 ⁽⁴⁾
p-Xylene	C_8H_{10}	156 ⁽²⁾	3.15 ⁽⁴⁾
m-Xylene	C_8H_{10}	146 ⁽²⁾	3.20 ⁽⁴⁾
o-Xylene	C_8H_{10}	170 ⁽²⁾	2.77 ⁽⁴⁾

Sources:

- (1) McAuliff, 1966
- (2) Sutton and Calder, 1975
- (3) Lyman *et al.*, 1990
- (4) Chiou *et al.*, 1989
- (5) estimated in accordance with procedures in Lyman *et al.*, 1982
- (6) Budvari, 1989

As they move away from the source, dissolved gasoline constituents are affected by advection, dispersion, sorption, volatilization at the capillary fringe, and biological or chemical transformation. Dispersion reduces peak concentrations, providing some natural attenuation, but it also increases the volume of the subsurface that is contaminated. Sorption slows the bulk migration rate of the solutes. Volatilization transfers the contaminant problem to the soil gas, and is probably not an important mass removal mechanism for the dissolved phase below the water table. Chemical and biological transformations are the only processes that provide permanent removal of contaminant mass from the environment.

Near an oxygenated gasoline source, high concentrations of methanol have the potential to increase the levels of BTEX in groundwater by cosolvency effects, but such increases are not expected for MTBE fuels (API, 1991). Elevated BTEX solubilities could increase the mobility of these contaminants, since sorption and solubility are generally inversely related

for nonionic organic compounds (Chiou *et al.*, 1979). Oxygenates could also affect the long term fate of BTEX in groundwater systems by inhibiting biotransformation of these compounds.

Research has shown that the limiting factor in BTEX persistence in groundwater is biodegradation (Barker *et al.*, 1989). The monoaromatics are biotransformed under a wide range of environmental conditions (Gibson and Subramanian, 1984). In aerobic groundwater, if oxygen does not become limiting, the biodegradation rate is rapid and no toxic breakdown products are found (Barker *et al.*, 1987). Conversely, anaerobic biodegradation of BTEX has been shown to occur at a significantly slower rate. In natural gradient injection experiments in a shallow, aerobic sand aquifer, BTEX has been found to persist only in oxygen-depleted zones (Patrick *et al.*, 1986).

Methanol is considered to be a readily biodegradable compound (White, 1986), and could potentially act as a preferred substrate in the groundwater environment. The oxygen demand exerted by high concentrations of methanol within a gasoline plume could cause rapid oxygen depletion, limiting oxygen availability and thereby increasing BTEX persistence. Little is known about MTBE biodegradation, but ethers are generally considered to be recalcitrant (Harada and Nagashima, 1975; Ludzack and Ettinger, 1960), so MTBE is unlikely to represent a preferred substrate.

Other inhibitory effects are also possible. For example, high concentrations of either of the oxygenates could harm microbial communities that degrade BTEX. In their review of the effects of alcohols on microorganisms, Ingram and Buttke (1984) report that alcohols can inhibit microbial cell function by partitioning into the cell membrane, causing increased leakage of ions and metabolites and decreased growth rates. Ethers, since they are also polar compounds, may behave similarly.

Regardless of mechanism, the inhibition of BTEX biodegradation by methanol or MTBE could lengthen the interval of time that BTEX remains in groundwater before natural

remediation occurs. Enhanced mobility of BTEX in groundwater could lead to longer transport distances over a given time period. Either occurrence would be undesirable because of the greater likelihood that BTEX from gasoline spills would reach drinking water supplies or environmentally sensitive discharge sites.

STUDY APPROACH

The natural gradient tracer test was conducted in a shallow, aerobic sand aquifer at Canadian Forces Base (CFB) Borden, Ontario. Pulses of groundwater contacted by each of the three fuels were simultaneously released below the water table. Chloride served as a conservative tracer. BTEX, oxygenate, and chloride concentrations were monitored for sixteen months using a dense network of multilevel samplers. Solute concentration data were reduced to plume-scale estimates of the location, mass, and degree of spreading of the solute plumes using spatial moment analysis. The subsurface mobility of BTEX and the oxygenates was defined by comparison with the conservative tracer. Effects of the oxygenates on BTEX migration and fate were distinguished by comparison to the control case, which contained no additives. Dissolved oxygen measurements were taken to investigate the role of oxygen availability in the fate of the organic solutes.

Laboratory microcosm experiments were performed to assess the ability of the microbial population at the CFB Borden test site to degrade BTEX and the oxygenates. The biotransformation process was isolated through the use of sterile controls. The microcosm experiments also explored the role of oxygen availability and oxygenate presence as constraints on BTEX metabolism. The laboratory work provided an assessment of biotransformation potential under static conditions, while the field experiment afforded an opportunity to examine biotransformation in a dynamic system in which solute transport phenomena in large part control the persistence of the compounds.

Section 2

THE BORDEN TEST SITE

The field site is located in an inactive sand quarry at Canadian Forces Base (CFB) Borden near Alliston, Ontario, Canada. A location map and cross section of the site are provided in Figure 2-1. The base of the quarry is sparsely vegetated and relatively flat, and measures about 100 by 250 meters. A leachate plume emanating from an abandoned landfill extends beneath the test site. Chemical solutions were injected into an aerobic, uncontaminated groundwater layer above the leachate zone. The sand aquifer at the site is analogous to those favored for public water supply in the glaciated northeast (Back *et al.*, 1988).

The site was originally instrumented for a large-scale tracer study of inorganic and halogenated organic compounds (Mackay *et al.*, 1986), and has since been used for two tracer tests with monoaromatic gasoline components (Patrick, 1986; Berry-Spark, 1987), so the hydrologic regime is well understood. Laboratory work performed in conjunction with the field studies has yielded detailed information about the aquifer medium. This section summarizes the physical and chemical features of the Borden experimental site.

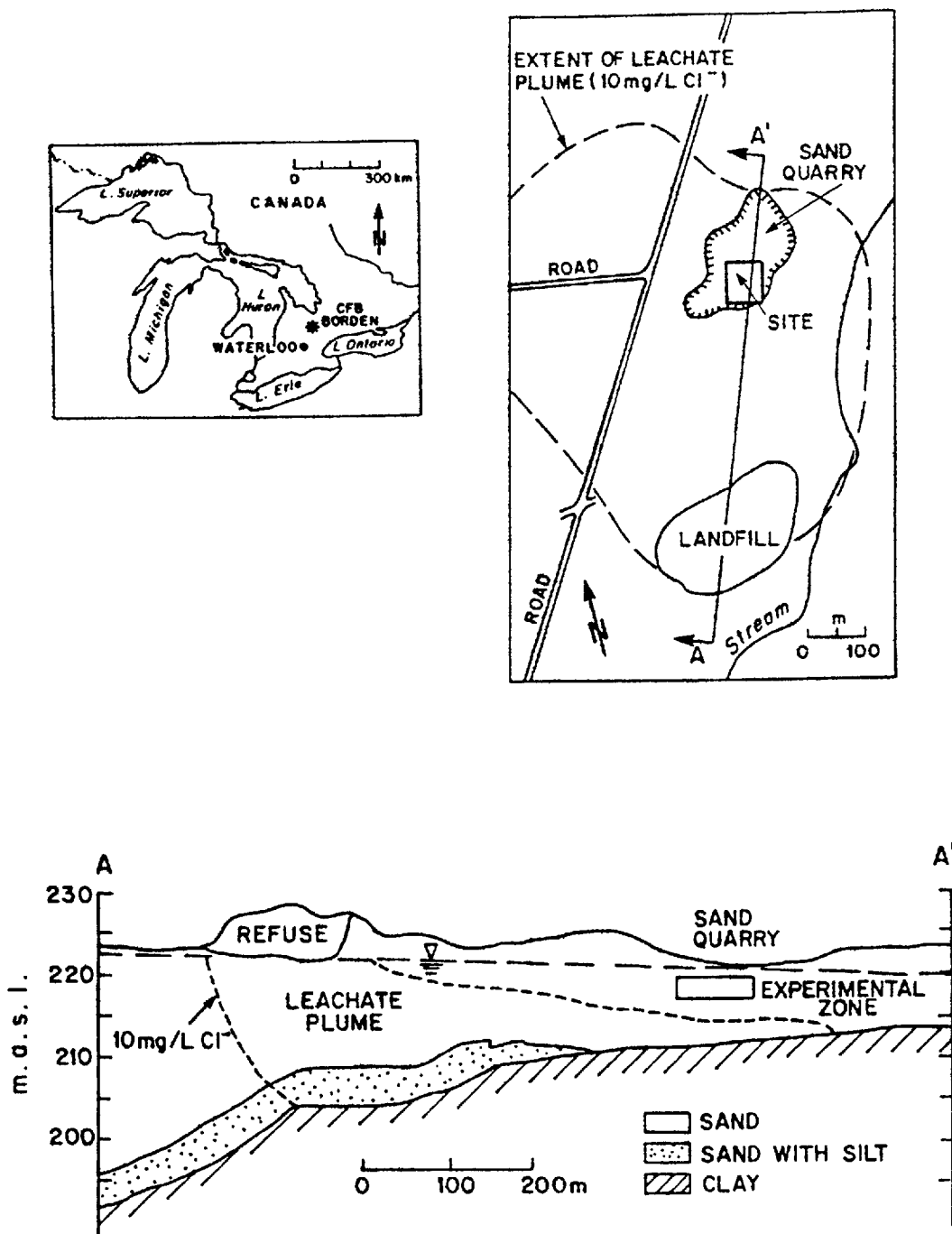


Figure 2-1. (a) Map of southern Ontario and the Great Lakes showing the location of CFB Borden; (b) Plan view of the test site in the Borden sand quarry showing the 1979 boundaries of the landfill leachate plume; (c) Site cross section showing the injection zone (after Mackay *et al.* 1986).

2.1 Geology

The aquifer at the test site is a glaciofluvial deposit composed of horizontal discontinuous layers of medium to fine-grained sand (Bolha, 1986). Horizontal lenses of coarse sand and silty clay are also present. The effective size of the lenses is about 0.1 m thick by 1.5 m to 3 m long (Sudicky, 1986). The aquifer extends from ground surface to about nine meters depth, and overlies a pebbly clay till (Bolha, 1986).

Quartz and feldspars are the predominant minerals in the aquifer material. Amphiboles and carbonates are also present. Rock fragments containing significant quantities of carbonate (as micrite/biomictite and sparite/biosparite) are found primarily in the coarser particle fractions. Amphiboles and accessory minerals such as augite, zircon, and magnetite/ilmenite are concentrated in the finer fractions. Many of the mineral surfaces are coated with a brown-orange coating, believed to be comprised of amorphous oxyhydroxide (Ball *et al.*, 1990).

The aquifer material has a low clay-size fraction, a small cation exchange capacity, and a small fraction of organic carbon (Table 2-1). Like many sand aquifers used for water supply, its capacity for attenuation of reactive solutes is relatively small.

2.2 Hydrogeology

Characteristics of the Borden aquifer are listed in Table 2-1. The aquifer is unconfined, with a water table that fluctuates seasonally over an interval of about 0.5 to 1.5 m below ground surface. In some portions of the sand quarry, the water table breaches land surface during storm events, but standing water has not been observed in the test area used for this experiment.

The horizontal hydraulic gradient ranges from 0.0035 to 0.0054, and averages about 0.0043. The gradient is oriented toward the northeast, and its direction varies seasonally over about 14 degrees (Sudicky, 1986). Changes in the magnitude and direction of the

Table 2-1. Characteristics of the Borden Aquifer

PROPERTY	ESTIMATED MEAN
Water Table Elevation	220.5 m MSL (1)
Hydraulic Gradient	0.0043 (2)
Flow Direction	N47E (2)
Average Linear Velocity	0.091 m/day (3)
Hydraulic Conductivity (K)	6 m/day (2)
K Correlation Scales:	
Horizontal	2.8 m (2)
Vertical	0.12 m (2)
Porosity	0.33 (3)
Particle Density	2.71 g/cm ³ (4)
Bulk Density	1.81 g/cm ³ (4)
Apparent Dispersivity:	
Longitudinal	0.36 m (5)
Horizontal Transverse	0.037 m (5)
Vertical Dispersion Coefficient	10 ⁻⁶ m ² /day (2)
Specific Surface Area	2.9 m ² /g (4)
Clay-Size Fraction	0.4% (4)
Cation Exchange Capacity	0.67 meq/100 g (4)
Organic Carbon Content	0.021% (4)
Calcium Carbonate Content	15.4% (4)

Sources: (1) Patrick, 1986 (4) Ball *et al.*, 1990
(2) Sudicky, 1986 (5) Freyberg, 1986
(3) Mackay *et al.*, 1986

gradient are thought to result from variable recharge at the upgradient landfill (MacFarlane *et al.* 1983). Vertical gradients at the site are negligible (Mackay *et al.*, 1986).

The spatial variability of the hydraulic conductivity distribution has been investigated in detail by Sudicky (1986). Hydraulic conductivities of the aquifer average about 6 m/day and range over two orders of magnitude. The calculated isotropic correlation lengths for hydraulic conductivity are 2.8 meters in the horizontal direction and 0.12 in the vertical (Sudicky, 1986).

Estimates of the average linear groundwater velocity range from 0.005 m/day to 0.1 m/day. Freyberg (1986) analyzed the movement of a nonreactive tracer over a 2-year period and reported a velocity of 0.091 m/day. The bulk effective porosity of the sand has been determined to be 0.33 (Ball *et al.*, 1990), although porosity estimates vary and have been reported as high as 0.38 (Sudicky, 1983).

Aquifer dispersivities have been calculated by Freyberg (1986) and by Sudicky (1986). The apparent longitudinal macrodispersivity is about 0.36 m, and the horizontal transverse dispersivity is about 0.037 m. In the vertical direction, dispersion occurs at the scale of molecular diffusion.

2.3 Groundwater Chemistry

The lower three to four meters of the aquifer are occupied by a landfill leachate plume (MacFarlane *et al.*, 1983). The groundwater in this zone is anaerobic and is characterized by high concentrations of sulphate, sodium, and chloride. The upper four to five meters of the aquifer, the zone in which the natural gradient tracer test was conducted, is aerobic and uncontaminated.

The inorganic chemistry of the aerobic zone of the Borden aquifer has been described by various researchers (e.g. Nicholson *et al.*, 1983; Mackay *et al.*, 1986; Agertved *et al.*, 1992). Table 2-2 presents a compilation of key compounds and their concentration ranges. In general, the upper aquifer has a neutral PH and low levels of nitrate and dissolved organic carbon. Background chloride averages about 2 mg/L.

The average temperature of the shallow groundwater is 10°C. Although the subsurface temperature ranges from 6°C to 15°C seasonally, there is no more than a 2°C difference with depth at any given time (Mackay *et al.* 1986). Spatial variability in temperature is therefore unlikely to measurably influence biotransformation rates in the aquifer.

Table 2-2. Chemistry of the Aerobic Zone of the Borden Aquifer

PARAMETER	CONCENTRATION RANGE (mg/L)
Calcium	50 - 110
Magnesium	2.4 - 6.1
Sodium	0.9 - 2.0
Potassium	0.1 - 1.2
Alkalinity as CaCO ₃	100 - 250
Chloride	1 - 3
Sulphate	10 - 30
Nitrate	< 0.6 - 0.7
Total Dissolved Solids	380 - 500
Dissolved Organic Carbon	0.7 - 15.8
Dissolved Oxygen	< 1.0 - 8.5
PH	7.2 - 7.9
Temperature (°C)	6 - 15

Sources: Nicholson *et al.*, 1983
Mackay *et al.*, 1986
Agertved *et al.*, 1992

2.4 Subsurface Microbiology

Berry-Spark (1987) performed viable aerobic plate counts on cores taken from the test site and reported bacterial populations on the order of 10^5 colony forming units (CFU) per gram of sand. Subsurface microbial populations ranging from 10^4 to 10^6 bacteria per gram of sand have been reported for other shallow sand aquifers (Ghiorse and Balkwill, 1983; Wilson *et al.*, 1983a).

Barbaro (1992) studied the microbial population in the upper three meters of the Borden aquifer at a location adjacent to the test site. She found a high diversity in the microbial population (38 taxonomic groups were isolated), but relatively low numbers of organisms (10^2 - 10^3 CFU/g aquifer material). Bacteria from five out of the 38 taxonomic groups isolated were able to degrade BTEX.

Microbial activity was found to be greatest at a depth interval of 1.55 m to 2.05 m below ground surface. Dissolved oxygen availability correlated positively with both microbial

counts and activity. Barbaro also identified a threshold dissolved oxygen concentration of 3 mg/L, below which the counts and activity of the aerobic microbial populations were negligible. Such zones may not support aerobic biodegradation of injected BTEX, even after both oxygen and BTEX are introduced into these zones, until after an active aerobic biomass is established. An acclimation period may be required for this to occur. Barbaro also observed greater microbial activity in zones of high hydraulic conductivity, although there were insufficient data for a statistical correlation.

Barbaro determined that the organic carbon levels in the Borden aquifer are sufficient to support active microbial populations, but that nitrogen may be a limiting nutrient. Other macro and micro nutrients have not been tested. Wilson *et al.* (1983b) have suggested that bacteria from nutrient-poor settings such as the aerobic zone of the Borden aquifer are oligotrophic and may be specialized in the capture of metabolizable organic compounds from very dilute solution.

2.5 Spatial Distribution of Dissolved Oxygen

Longitudinal profiles of dissolved oxygen distribution in the three injection zones of this study, shown in Figure 2-2, were taken one week prior to the injection to establish background conditions. A fourth profile, shown in Figure 2-3, was taken transverse to the expected plume locations to provide a three-dimensional understanding of the spatial distribution of oxygen in the upper aquifer.

The sections show a natural zone of lower dissolved oxygen (1-2 mg/L) at the elevation of the injection. Patrick (1986) observed a similar zone of low oxygen. The zone contains a series of discrete lenses with oxygen levels less than 2 mg/L. The lenses are typically 2 meters in length and width, and about half a meter thick. They are at the same scale as the aquifer sand beds, and it is possible that the spatial patterns of dissolved oxygen are related to the hydraulic conductivity distribution.

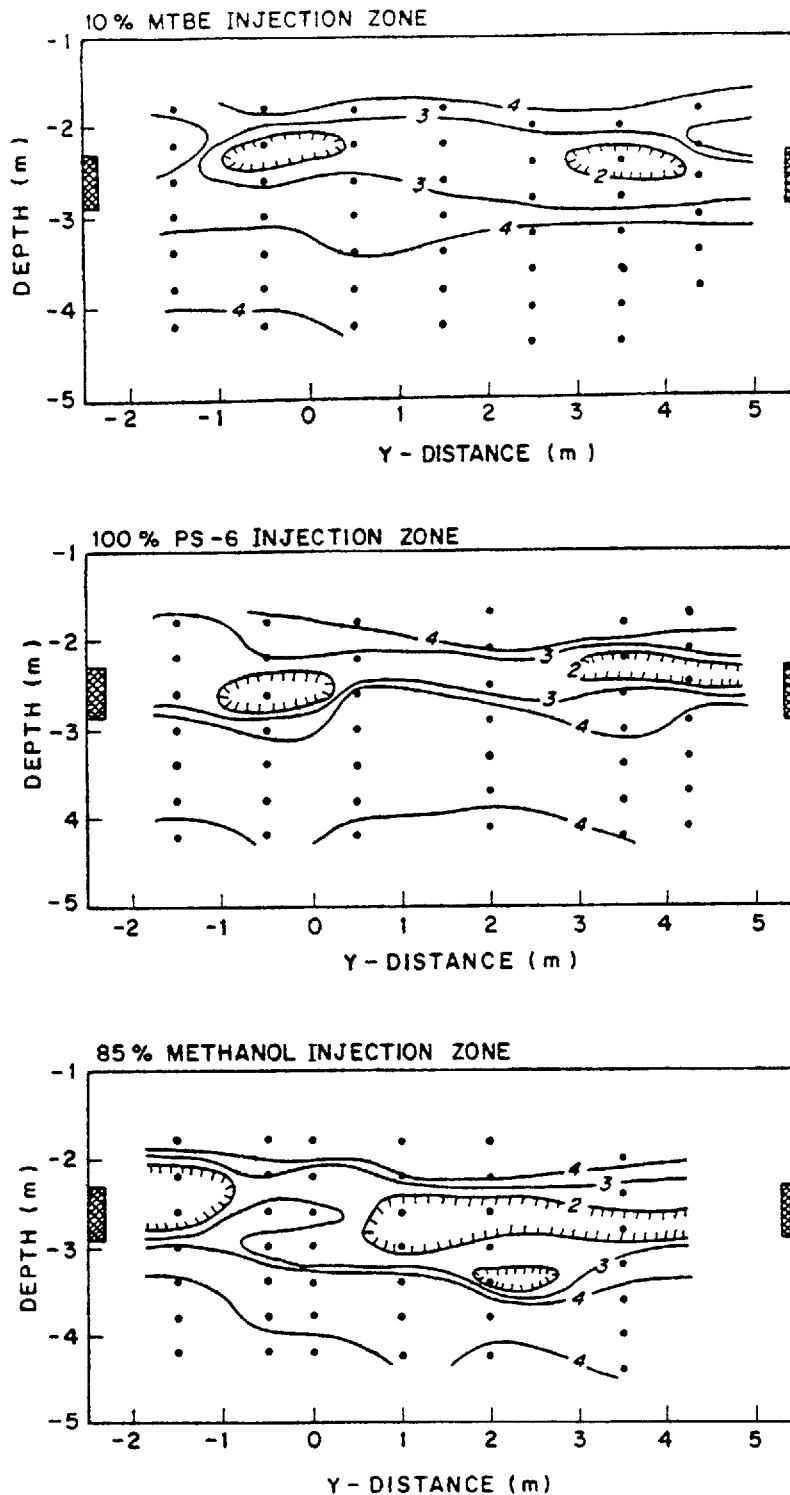


Figure 2-2. Longitudinal profiles of background dissolved oxygen distribution for the three injection zones. The injection interval is shown for reference.

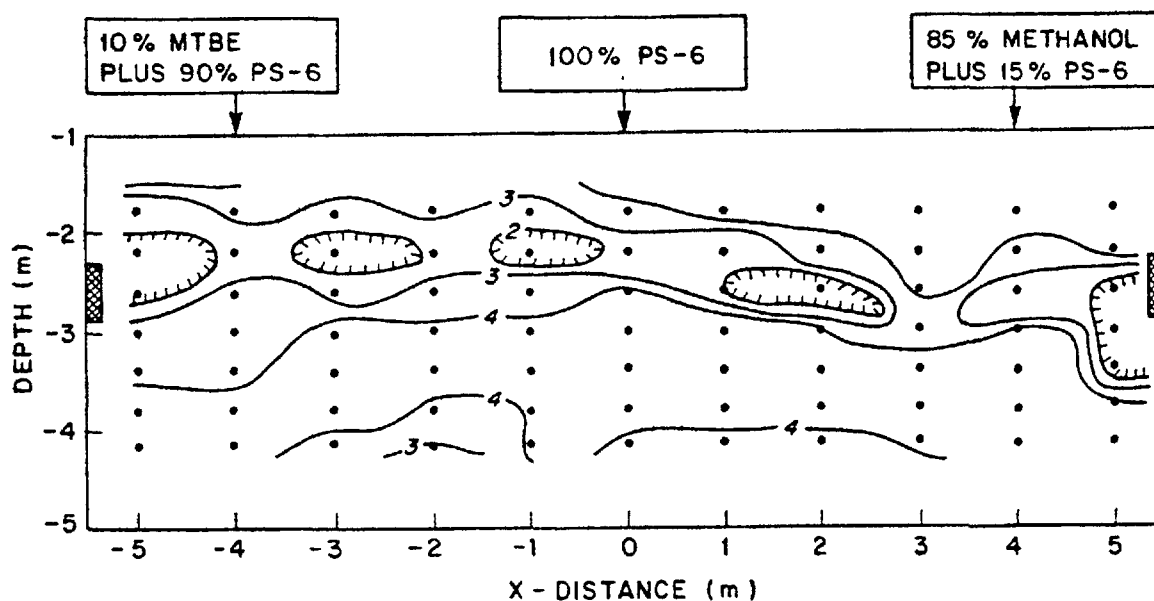


Figure 2-3. Transverse profile of background dissolved oxygen distribution at the three injection zones. The injection interval and points of injection are shown for reference.

None of the sampled points were entirely devoid of oxygen, although two were below 1 mg/L (not shown), and it is likely that the upper aquifer contains anaerobic microsites. Dissolved oxygen did not approach its solubility level of 8-10 mg/L at any measured location, indicating that a metabolizable substrate, such as naturally occurring organic carbon, is exerting an oxygen demand in the subsurface.

It is evident from the cross sections that the distribution of background dissolved oxygen is similar in the three injection zones. Availability of background oxygen, required for aerobic metabolism of the monoaromatic hydrocarbons, was therefore expected to be similar for the three plumes and did not represent an experimental variable.

Section 3

THE FIELD EXPERIMENT

The field experiment began in July 1988 with the injection of three solute pulses into the shallow Borden aquifer. Movement of the solutes was monitored by synoptic sampling of a multilevel piezometer network. Six sampling rounds were made over a sixteen month period, and more than 8,000 samples were collected. The controlled injection of the solutes ensured a well defined source condition, and in general, sampling yielded effective coverage of the solute distributions in three dimensions. This section outlines the design and procedures of the field injection, the monitoring approach, and the methods of sample collection and analysis.

3.1 Injection Solutions

The field injection solutions were designed to represent the composition of solute plumes emanating from spills of three fuel types:

- 100% gasoline (control)
- 90% gasoline plus 10% MTBE (v/v); and
- 15% gasoline plus 85% methanol (v/v).

A major goal for the study was to establish BTEX and oxygenate concentrations that would typify those occurring downgradient from inadvertent releases of these three fuels in a shallow sand aquifer. The desire for accurate representation of field concentrations was balanced by several scientific objectives, including provision of solute levels that were sufficiently high to ensure detectability over the test period, and establishment of equal BTEX levels for the three solutions to remove concentration as an experimental variable. A chloride tracer was included in each solution as a conservative tracer of solute movement in the subsurface.

The injection solutions were prepared by contacting groundwater with gasoline and diluting to representative field concentrations. To ensure constancy of fuel composition, an unleaded gasoline, PS-6, was provided by the American Petroleum Institute. The

oxygenates were spectranalysed methanol and analytical grade MTBE. Chloride was added in the form of sodium chloride. Site groundwater, extracted from the same depth as the injection zone to ensure a similar chemistry, was used as the solvent.

PS-6 gasoline probably contains about 1,200 compounds, with 151 identified by Brookman *et al.* (1985). Forty-two of the identified compounds comprise about 75% of the mass that dissolves when PS-6 gasoline contacts water. BTEX makes up about 15% of the PS-6 gasoline volume, and constitutes up to 60% of the mass that goes in solution. Aside from BTEX, water contacted by PS-6 gasoline also contains other methylated benzene isomers, methylated phenol isomers, and short-chain aliphatic compounds, with varying proportions depending on the particular gasoline blend.

API (1991) studied the composition of solutions obtained from contacting PS-6 gasoline and oxygenate blends with water. At the 10:1 phase ratio, all three fuel-contacted waters contain about 115-120 mg/L total BTEX. Water equilibrated with the 85% methanol fuel contains about 62,000 mg/L methanol, and water equilibrated with the 10% MTBE fuel contains about 3,600 mg/L MTBE. These levels are representative of what might be found in groundwater that is in direct contact with a gasoline source.

The purpose of this experiment was to simulate solute behavior in plumes that have traveled some distance from the source. Consequently, in designing the injection solutions, target concentrations of the solutes were set at levels ten times smaller than the expected saturation concentration. The target concentrations were 15 mg/L for total BTEX, 6,000 mg/L for methanol, and 350 mg/L for MTBE.

Case studies at gasoline spill sites indicate that BTEX levels typically range from 10 to 20 mg/L (API Soil Groundwater Task Force, pers comm). Few case studies of MTBE contamination of groundwater were available when the study was initiated, but levels of up to 236 mg/L were observed at a gasoline spill site in Maine (Garrett *et al.*, 1986). Case studies of contamination by methanol-bearing fuels were not available. Based on the

available case histories, the target concentrations set for this experiment were considered representative.

A target chloride concentration of 500 mg/L was selected for each of the solutions because it was high enough to remain well above background levels over about a two year period, and low enough to preclude significant density differences with background groundwater early in the experiment.

3.2 Injection Well Configuration

A key objective of the experiment was to create three plumes of similar size that would travel side by side in the same flow system and geochemical environment, with minimal lateral overlap. Based on the constraints of the existing monitoring network at the site, solute pulses with a length of 3 meters, width of 2 meters, and thickness of about 1.5 meters were planned. With these dimensions, each pulse would occupy about 9 cubic meters of the aquifer and contain about 3,000 liters of solution, assuming an aquifer porosity of 0.33.

It should be noted that in the case of accidental gasoline spills, releases of equivalent volumes of the three fuel blends would produce different size solute plumes since more BTEX mass is available in 100% gasoline than in the two fuels containing oxygenates. For this experiment, three plumes of identical size were required to ensure comparability of solute migration and fate.

Nine injection wells were used. Their configuration is shown in Figure 3-1. Three wells spaced 1 meter apart and aligned parallel to the flow direction were provided for each pulse. Wells for each pulse were separated by only 4 meters to ensure that the initial solute plumes would remain within the domain of the monitoring network. Significant lateral overlap of the plumes at late times was not expected because of the small horizontal transverse dispersivity of the aquifer.

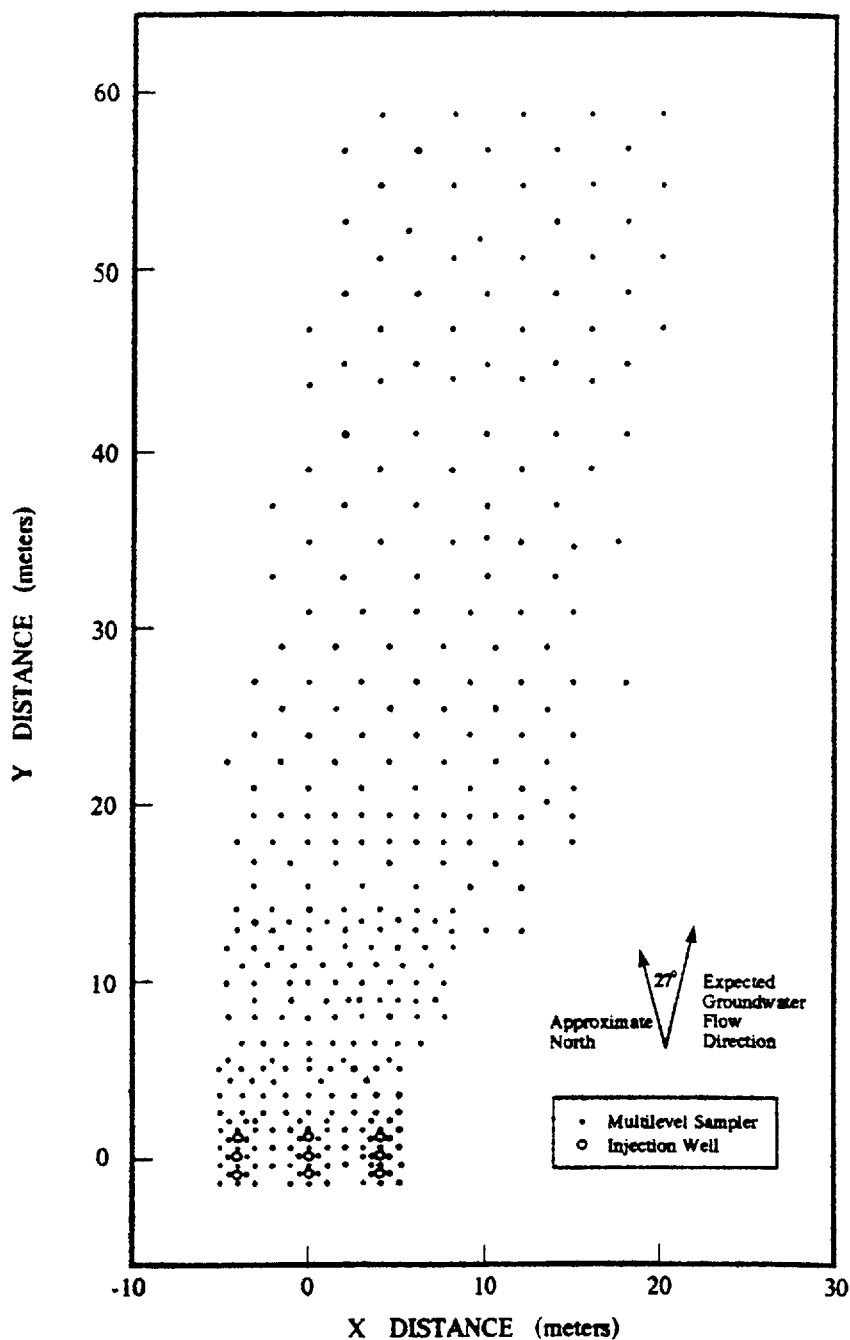


Figure 3-1. Plan view of the final array of multilevel samplers, and locations of the injection wells. The 10% MTBE pulse was injected on the left (1), the 100% PS-6 control pulse was injected in the center (2), and the 85% methanol pulse was injected on the right (3).

An injection zone depth interval of 2.29 to 2.90 meters below ground surface (about 1.3 m below the prevailing water table) was considered optimal. Release of the solutions at this distance below the water table ensured that the top of the solute pulses would be well below the air-water interface, thereby precluding mass losses by volatilization. The injection zone was also considered to be shallow enough to minimize interference with the landfill leachate plume below the site over the course of the experiment.

3.3 Solute Injection System

The injection system was designed by Karen Berry-Spark of Beak Consultants. The injection apparatus was patterned after those used for previous tracer tests at the Borden site (Mackay *et al.*, 1986; Patrick, 1986; and Berry-Spark, 1987). The purpose of the system was to mix the three chemical solutions onsite and provide the desired BTEX, chloride and oxygenate concentrations. The system also had to provide simultaneous releases of 3,000 L of each of the three solutions to the subsurface with minimal disturbance of the natural flow field. Furthermore, the system was designed to produce a relatively uniform distribution of the solutes of concern throughout each plume as an initial condition.

Basic principles of its operation were as follows: site groundwater was extracted, stored in a reservoir, mixed with PS-6 gasoline-saturated water at a 10:1 (v/v) ratio, spiked with the appropriate chloride and oxygenate solutions, and injected at the three locations.

Major system components included a groundwater source well, two groundwater reservoirs, a gasoline saturator, three containers for addition of chloride and oxygenates, three mixing vessels, and the nine injection wells. A schematic diagram of the system and details of its operation are provided in Appendix A. The system was sealed to prevent volatilization, and the organic solutes primarily contacted weakly sorbing surfaces such as Teflon prior to injection. The system was field tested before the experiment began.

3.4 Injection of the Solutes

On July 13, 1988, approximately 8.5 cubic meters of solution were injected into the aquifer (about 2,835 liters for each pulse) over a 12-hour period. The solutions were injected for 9 hours at a flow rate of 1.5 L/hour and for 3 hours at a flow rate of 0.75 L/hour. The source well was located about 100 meters north of the injection zone, and its screen spanned the same depth interval as the injection wells.

Samples of the injection solutions were taken at approximately 50 minute intervals from three inline ports located immediately in advance of the injection wells. They were analyzed for BTEX, oxygenates, chloride, PH, and temperature. Samples were also taken from these ports for dissolved oxygen analysis at half hour intervals. Once the injection was over, the nine injection wells were removed to ensure that no water remained behind in the standpipes. The aquifer sand collapsed into the boreholes following removal.

3.5 Results of Injection Monitoring

Average solute concentrations for the three injection solutions are shown in Table 3-1. The average concentrations essentially met the target levels for total BTEX, chloride, and the oxygenates. Average levels of BTEX, dissolved oxygen, PH and temperature were similar in all three solutions, ensuring comparability of solute behavior for the three pulses.

Results of the injection sampling are tabulated in Appendix A. The coefficients of variation for total BTEX concentrations in the injection solutions over time were 40% for the PS-6 pulse, 28% for the 85% methanol pulse, and 55% for the 10% MTBE pulse. Dissolved oxygen in all three solutions began at levels of about 7-8 mg/L and dropped to concentrations below 1 mg/L after about 5 hours of injection.

Table 3-1. Average Solute Concentrations in the Injection Solutions (mg/L)

Solute	90% PS-6 10% MTBE	100% PS-6	15% PS-6 85% Methanol
Chloride	515.0	479.0	577.0
Methanol	-----	-----	7,034.0
MTBE	289.0	-----	-----
Benzene	7.67	7.20	7.73
Toluene	5.35	4.95	5.16
Ethylbenzene	0.96	0.80	0.82
p-Xylene	0.96	0.81	0.80
m-Xylene	2.46	2.03	2.08
o-Xylene	1.38	1.18	1.17
BTEX	18.43	16.98	17.76
Dissolved Oxygen	2.27	2.55	3.07
Temperature °C	18.5	18.2	19.3
PH	6.91	6.94	6.97

3.6 Multilevel Sampler Array

The Borden site was instrumented with multilevel piezometers for the previous tracer tests, so a network of 110 of these devices was available before the experiment began. Prior to the injection, additional samplers were installed to increase the density of sampling points around the planned injection locations. As the experiment progressed, further additions to the monitoring network were made to accommodate the advancing plumes.

Figure 3-1 shows a schematic plan view of the final array of multilevel samplers. The network was about 20 m wide and 60 m long, and spanned a depth interval of about 4.5 m. It included a total of 335 multilevel samplers arranged in 47 rows, with 4,788 sampling points. The horizontal spacing of the piezometers varied from 0.25 m near the injection wells to 4 m at the downgradient boundary of the grid.

The multilevel samplers have been described by Mackay *et al.* (1986). A schematic diagram of a typical piezometer from this study, and a table of specifications for the sampling devices, are provided in Appendix B. Each sampler consists of a series of 3.2 mm O.D. flexible Teflon tubes connected to a 13 mm O.D. rigid PVC center stalk. The tube ends are screened with Nytex nylon and are vertically separated at 0.2 m or 0.3 m intervals. The horizontal and vertical distances between sampling points are compatible with the scale of the structural bedding in the Borden aquifer, and with the calculated hydraulic conductivity correlation lengths.

3.7 Monitoring Approach

Eight organic compounds were monitored during the experiment: benzene, toluene, ethylbenzene, para, meta, and ortho-xylene, MTBE, and methanol. Chloride was sampled at the same points as the organics. Dissolved oxygen was measured in longitudinal sections through the plume centerlines. Water samples were collected from subsets of the multilevel sampling network beginning six days after the injection. Sampling rounds were performed as quickly as possible in order to obtain "snapshots" of the three dimensional solute distributions. The plumes were sampled six times in sixteen months.

For each round, sample points were chosen based on contour plots of previous plume locations and predictions of solute migration rates. The plumes were consistently sampled inward from the north and south ends. Laboratory analyses for the organics were rapid, so data from samples taken in the first two days of a sample event were available for field decision making. The preliminary organics data were used to ensure that the plume margins had been captured. Wherever possible, piezometers with background levels of the solutes were sampled around each plume.

Table 3-2 summarizes the six sampling sessions. The sample events ranged from two days for the early rounds to eight days for the fourth sample round, in which the greatest number of samples was collected. The solutes being tracked separated over time and

occupied an increasing volume of the aquifer. Thus, even though the density of the network decreased with distance from the source, a large number of samples was required at late times to delineate all of the plumes. More than 8,000 samples were collected for chloride and organics analysis over the course of the experiment.

Table 3-2. Summary of Sampling Rounds.

Sample Round	Sample Dates	Time Since Injection (days)	Number of Wells Sampled	Number of Points Sampled	Number of Data Points
Injection	07-13-88	0	--	--	--
1	07-18-88 to 07-20-88	6	86	860	7,740
2	08-22-88 to 08-25-88	42	112	1,120	10,080
3	10-24-88 to 10-29-88	106	88	880	7,920
4	05-23-89 to 05-30-89	317	172	1,740	15,660
5	08-14-89 to 08-17-89	398	154	1,730	15,300
6	10-30-89 to 11-03-89	476	155	1,700	15,300
TOTAL		476	767	8,030	72,270

NOTE: Number of points sampled and number of data points are estimates.

Dissolved oxygen sampling was conducted one week prior to the injection and then in the week following each sampling event. Profiles were made along the plume centerlines, and generally extended several meters behind and in front of the organics plumes. To reduce the time required for field analysis, dissolved oxygen measurements were made at

alternating piezometer points. Over 2,500 dissolved oxygen analyses were performed during the experiment.

3.8 Collection and Analysis of Water Samples

Samples for organics and chloride were taken using two sampling manifolds equipped with peristaltic pumps. Each manifold was capable of sampling fourteen tubes of a given multilevel piezometer simultaneously. The manifolds were designed specifically for sampling multilevel piezometers for volatile organic compounds and chloride, and are a modification of those described in Mackay *et al.* (1986). Appendix C includes a detailed description of sampling procedures and a schematic diagram of the sampling device.

Groundwater samples were collected directly into 18 ML glass hypovials for organics analysis, and into 20 ML polyethylene bottles for chloride analysis. To prevent biotransformation of the monoaromatics in the sample vials, 0.1 ML of a 10% sodium azide solution (v/v) was added to each hypovial with a syringe prior to capping. The samples received no exposure to the atmosphere except for a few seconds while the azide was added, and the vials were capped with Teflon-lined silicon septa.

About 50 ML of water flowed to waste per sample (about three times the tube volume), which ensured that each piezometer tube and the sampling system were thoroughly flushed. In total, about 100 ML of groundwater was extracted per point. If the withdrawal zone is assumed to be spherical, its radius would be about 8.5 cm. Less than two percent of the plume mass is estimated to have been removed during sampling.

Samples intended for organics analysis were stored with icepacks in insulated coolers and transported to the University of Waterloo Earth Sciences Laboratory for analysis at the close of each sampling day. They were stored at 4°C until analysis. Laboratory analytical procedures for the compounds and quality control results are discussed in detail in Appendix D. The monoaromatics were analyzed by hexane extraction followed by gas chromatography, and the oxygenates were analyzed by direct aqueous injection onto a gas

chromatograph. Detection limits were about 2 µg/L for the monoaromatics and about 250 µg/L for the oxygenates. All organics analyses were performed within fourteen days of sample collection. Chloride levels were determined with an Autoanalyzer, and the detection limit was 1.5 mg/L. A set of blind controls was included in the final sample event. Dissolved oxygen was measured at the field site using the azide-modified Winkler technique (APHA, 1985). The detection limit for dissolved oxygen was about 0.2 mg/L.

3.9 Quality of the Solute Concentration Data

In order to reduce laboratory analytical costs and keep the duration of sample events to a minimum, field duplicates were not collected in this study. However, the quality of the concentration data are expected to be similar to that of Patrick (1986), since identical field and lab procedures were used. In his study, Patrick found a relative standard deviation of 5%-10% in concentration values for field duplicates, and a -5% bias in the monoaromatics data from sampling with the manifold.

Equipment blanks were taken during the fifth sample round of this study in order to test the potential for cross contamination during sampling. The analytical results, provided in Appendix C, indicate that there is some minor potential for cross contamination, and that in future experiments field quality control procedures should be performed more routinely to aid in data interpretation. In this study, piezometers around the margins of the plumes typically had no detectable monoaromatics, indicating that cross contamination was relatively rare. Furthermore, in an experiment of this magnitude in which plume-scale observations of solute behavior are emphasized, minor cross contamination problems are unlikely to significantly affect overall data interpretation.

Section 4

DATA MANAGEMENT AND ANALYSIS

A substantial data set was generated during the natural gradient tracer test. Over 72,000 individual concentration values had been obtained by the end of the experiment. The primary goal of the data manipulations undertaken in this study was to reduce these point concentration data to a form that permitted plume-scale comparison of the organic solutes to the nonreactive tracer for each of the three test cases. The method of Freyberg (1986) was adopted because it provides plume-scale estimates of solute mass, center of mass, and spreading parameters. Furthermore, his technique had been used for two previous natural gradient experiments with gasoline constituents, and was readily available.

Freyberg's method entails vertical integration of the three dimensional concentration data, projection of the integrated data onto a regular grid, and estimation of the zeroth, first, and second spatial moments, which correspond to the mass, center of mass, and spatial covariance of the concentration distributions. Since biotransformation was expected to be the key controlling process in BTEX persistence in the plumes, the primary focus of the data analysis was on obtaining accurate estimates of solute mass.

Throughout the analysis, a descriptive understanding of the structure of the solute plumes was emphasized: hand-contoured cross sections and maps served as a basis for much of the interpretation. Although this approach is time-consuming, it is essential to a thorough understanding of solute behavior and served as an important qualitative check on spatial moment estimates.

This section outlines procedures used in this study to correct data to accurately reflect field conditions and to obtain spatial moment estimates. It also comments on issues of data quality and identifies potential sources of error. Bringing the solute concentration data from its raw form to the plume-scale estimates of transport and fate parameters involves multiple stages, all of which require interpretation and can introduce uncertainty.

The estimates produced here are by no means definitive. They can be refined and sources of error can be explored more fully in future work with the data.

4.1 Data Entry and Correction Procedures

Concentration data for the organic solutes were electronically recorded on chromatogram printouts and hand recorded on data forms during sample analysis. Data from the forms were typed onto personal computer (PC) spreadsheets and each concentration value was checked against the form for transfer error. The chromatograms were retained and used for reference in cases of apparently anomalous concentration values. Concentration data were transferred to a mainframe computer for subsequent manipulations. Data were corrected by subtracting laboratory blanks and removing concentrations that were below detection or background values, by removing data from sample points that were situated within the landfill leachate, and by interpolating missing values.

Blank Subtraction. At each analytical date, small quantities of some of the monoaromatics were found in laboratory blanks. These data are tabulated in Appendix D. On a typical day, three or four blanks were analyzed interspersed among about one hundred samples. Sample analysis times and order were not consistently recorded, so blanks could not be keyed to specific samples. It is common practice in such cases to average the blanks for a given date and subtract the average value from sample data analyzed on that date. However, blank contamination was only sporadically present, and subtraction of the average was insufficient to remove anomalous data corresponding to locations beyond the apparent plume boundaries.

The interpolation routines could not easily handle these anomalous data, so for convenience in data management the largest value of a blank for a given date was subtracted from sample data analyzed on that date. This method of blank subtraction is expected to have little consequence for overall data interpretation. It has potential to affect only the mass estimates for benzene, toluene and ethylbenzene, which appeared consistently in the blanks. For these plumes, it is possible that a small negative bias in

mass estimation has been introduced. However, the three injected plumes are expected to be equally affected, so comparisons remain valid.

Detection Limit and Background Removal. Following blank subtraction, all concentrations that were below the analytical detection limits were set to zero. A detection limit of 2 µg/L was used as a cutoff for the monoaromatics and 250 µg/L was used for the oxygenates. Chloride is present in the Borden aquifer at background levels averaging about 2 mg/L, so this value was used as a cutoff.

Removal of Landfill Leachate Data. Cross sections were made of chloride concentrations along the plume centerlines. They revealed obvious instances of chloride values in the lower points of the deeper multilevel piezometers which could not be part of the injected plumes, but rather represented interference with the landfill leachate plume below the site. Based on the cross sections, chloride data were removed from deep piezometer points where appropriate. None of the organic solutes was detectable at sample locations that extended into the leachate plume.

Treatment of Missing Data Points. For all of the sample rounds, there were occasional missing concentration values due to clogged piezometer screens and transport or lab breakages. In addition, for the first four sample rounds, piezometer points one, three, twelve, and fourteen were deliberately omitted from the sampling schedule in order to reduce laboratory analytical costs. Data from points above and below the missing points were linearly interpolated. In the case of missing data in the top and bottom points of the piezometers, the concentrations were assumed to reach background values within a distance equal to the vertical sampling interval.

4.2 Evaluation of Plume Capture

Data sets were checked for completeness both vertically and horizontally before use in the moments analysis, using cross sections of solute concentration data. In several cases, individual piezometers did not fully penetrate the solute clouds. In the first sample round,

the tops of many of the plumes tended to lie above the uppermost sampling ports, and in later sample rounds the more mobile solute plumes extended below the bottom of the sampling network.

Other researchers have approached the problem of incomplete vertical plume capture in various ways. Freyberg (1986) assumed concentrations reached background within a distance less than or equal to twice the vertical sampling interval for locations where the top or bottom sampling ports yielded concentrations greater than background. Garabedian *et al.*, (1991) linearly interpolated between neighboring piezometers to complete vertical profiles for cases where samplers did not fully penetrate the tracer clouds. In this study, concentration values were not extrapolated above the top sample ports, or below the bottom sample ports. The concentrations were assumed to reach background values within one vertical sampling interval above the top sample port and below the bottom sample port.

It was evident from the cross sections that the concentration distributions were nonuniform, particularly for the biodegrading solutes. In order to have some confidence in any horizontal interpolation between sample points, it would be necessary to examine data from each multilevel sampler in light of information available at all surrounding samplers. In many cases surrounding samplers did not contain enough information to make a valid judgment, since they spanned a similar depth interval. Options for interpolation in the case of incomplete plume capture in the horizontal transverse direction were especially limited because the plumes were narrow, with steep lateral concentration gradients, and few samplers intersected the plumes in the transverse direction.

Accordingly, such interpolation was not attempted. For future experiments in the same location, several deeper piezometers should be installed to use as reference points for horizontal interpolation, and the transverse resolution of the network should be improved.

Cross sections and plan view contour maps also gave an indication of the degree of horizontal plume capture. In general, capture was excellent along the sides of the plumes except for the 85% methanol case, which extended outside the domain of the network in

sample rounds two and three. The front and back ends of all three plumes were incompletely captured in the first three sample rounds.

Garabedian *et al.* (1991) placed fictitious samplers containing extrapolated data around plumes which were insufficiently captured prior to moment analysis. Their technique was not adopted for this study, but could be implemented in future work with the data. For this study, incomplete horizontal capture was managed by setting the limits of areal interpolation at the inferred location of the plume boundary. Plume maps and cross sections were used to choose appropriate plume boundaries, and transverse symmetry of mass distribution was assumed. Individual cases of incomplete plume capture are discussed in Section 7 in light of the certainty of the mass estimates.

4.3 Depth Integration of Solute Concentrations

After the data had been checked for completeness and corrected where necessary, concentrations were depth integrated. The integration process reduced the data to a two dimensional form, yielding one value for each solute at each piezometer for each sample time. Integration of vertical concentration data used trapezoidal quadrature represented by the following equation:

$$C = \frac{\Delta x}{2} (f_1 + f_n + 2\sum f_i)$$

where C = depth integrated concentration (mL^{-2})
 Δx = distance between sampling points on a multilevel piezometer (L)
 f_1 = solute concentration at top point (mL^{-3})
 f_n = solute concentration at bottom point (mL^{-3})
 f_i = solute concentration at intermediary points (mL^{-3})

The concentration distribution was integrated over the vertical distribution of each solute plume, yielding a depth-integrated concentration (mL^{-2}) for each piezometer that was representative of solute mass at that location. Integrating this vertically-integrated concentration data over the area of the plume (section 4.5) yields the total mass of solute present in the plume.

Using this method, the sample point spacing must be known for each piezometer in order to produce an accurate depth-integrated concentration value. The monitoring network used for this experiment represents an amalgamation of samplers from previous experiments and newly installed samplers. The piezometer specifications from previous experiments were not recorded systematically, so the point spacing of several samplers is not known with certainty: these are identified in Appendix B.

Depth integrated values for the solutes at each sampling event were plotted on a map of the piezometer locations and hand contoured. The maps were used to separate data for the three solute plumes under study. In general, there were sufficient zero values at piezometers between plumes to readily distinguish them from one another. In a few cases, particularly for chloride at late times, there was some lateral overlap. The oxygenates were useful as indicator compounds for delineating plumes for the three test cases.

4.4 Projection to a Regular Grid

The depth integrated concentration values for each piezometer location were projected onto a regular rectangular grid over the horizontal extent of each solute plume using the Surface II Graphics System Package of Sampson (1978). In total, data from 138 solute distributions were subject to the gridding routine. The Surface II package is designed to handle irregular arrays of data points. Selection of the estimating procedure for grid construction is user controlled. Options specified in the program include the desired grid size and grid node spacing, and the interpolation options. A discussion of the options chosen for analyzing the data for this experiment is provided in Appendix E. Once data are in the form of regularly spaced values, they can be contoured using the Surface II package, and/or the grid matrix generated by Surface II used in the estimation of spatial moments.

4.5 Spatial Moment Estimation

Spatial moment estimates for each solute concentration distribution were made for each sampling session. The spatial moment is an integrated measure of the concentration field

over the extent of the solute plumes, and is used to interpret plume-scale processes. The ij th moment of the concentration distribution in space, M_{ij} , is defined as:

$$M_{ij} = \iint n C(x,y) x^i y^j dx dy$$

where n = porosity

$C(x,y)$ = vertically-integrated concentration field

x,y = spatial coordinates.

The integration is over the x, y space.

The estimation procedure involves the application of an areal numerical quadrature routine to the grid matrix of vertically-integrated concentration data generated by Surface II (Section 4.4). This routine sums the integral of non-overlapping unit cells to derive the zeroth (i.e., $i + j = 0$), first ($i + j = 1$), and second ($i + j = 2$) spatial moments. It is further described by Freyberg (1986) and by Patrick (1986) and is based on the work of Aris (1956).

The zeroth moment provides a measure of the mass of a compound in solution. The first moment, normalized to the mass in solution, defines the coordinate location of the plume's center of mass. The second moment defines a spatial covariance tensor that is related to the spread of a concentration distribution about its center of mass. The first and second moments are normalized by the zeroth to obtain location and spreading parameters, so the mass estimate is most sensitive to estimation error. For example, since they are ratios, porosity cancels out of all parameter estimates except mass in solution. Furthermore, the mass of the plumes is the key parameter for understanding long term solute persistence. Therefore, the focus of this analysis has been on obtaining accurate estimates of solute mass.

4.6 Discussion of Sources of Error in Mass Estimation

There are several potential sources of error associated with estimating solute mass through time for pulse injection experiments. First, the concentration data must be of reasonable

quality: previous experience with natural gradient tracer tests using gasoline constituents suggests that concentration data tend to vary by only 5% to 10%. Volatile and sorptive losses during sampling may introduce a 5% negative bias for the monoaromatics (Patrick, 1986). Cross contamination using the manifold is expected to exert a minimal influence on mass estimation, and removal of contaminant mass during sampling and piezometer development is calculated to have been less than 3%. Laboratory blanks can introduce either a negative or a positive bias to the data, depending on how they are subtracted: in this study, the method of blank subtraction is more likely to introduce a small negative bias in mass estimation. All of the sources of error associated with the quality of the concentration data are expected to be consistent both among the three injected pulses, and from sample event to sample event.

Insufficient plume capture can lead to substantial underestimation of solute mass, but detailed cross sections can provide a qualitative understanding of capture, and correction methods are available (Garabedian *et al.*, 1991). Lateral overlap of adjacent plumes can also introduce error because the outer boundary of overlapping plumes must be defined by a larger concentration value in order to separately evaluate their masses. This error would be closely related to errors introduced by comparing plumes detectable to different ratios of the input concentrations, and can be canceled to some degree through data normalization.

Mackay *et al.* (1986) noted that spatial variability of porosity with distance along the plume travel path can lead to biases in mass estimation with time. However, no such systematic variation in porosity is expected at the Borden site. As noted by Patrick (1986), the depth integration procedure is unlikely to represent a significant source of error because the vertical distance between sampling points (0.2 to 0.3 m) is small relative to the thickness of the plumes (0.5 m to 2 m). However, vertical integration can introduce error when the point spacing is not known for all samplers.

For plumes that are fully captured by the monitoring network, and for which solute concentration data are considered reliable, Patrick (1986) suggested that the largest source of error in the estimation process is likely to arise from the areal interpolation routine of the Surface II programs. This is because the horizontal distance between sampling points is large relative to the area covered by the plumes. Patrick's observation also applies to this study.

This experiment differed from previous tests, in that the initial solute pulses were elliptical rather than spherical and the piezometer network was not regularly spaced but offset. Accurate areal interpolation was expected to be especially error prone for mobile solutes at late times. Such long, thin plumes developed that the plume width approached the lateral spacing of the piezometers, and there was some concern that the position of a plume in the monitoring network could have a significant bearing on our ability to accurately estimate the mass. For example, one sensitivity analysis of the mass estimation procedure saw a substantial positive error in mass estimation with increasing piezometer spacing. For a regular grid with 2 m spacing, an 80 % overestimation of the mass was observed. Since a key objective of this study was to compare the behavior of solute plumes for the three cases over time, it was necessary to have some assurance that mass estimation errors would be both small and comparable for all plumes regardless of their position in the monitoring network.

Patrick (1986) did a sensitivity analysis of the areal interpolation routine and identified several potential sources of error. His approach was to place an analytically generated plume with known moment values into a regularly spaced piezometer array, and derive moment estimates. He then compared the estimated moments to the known moments to get an indication of the magnitude of the estimation errors.

For this study, Patrick's method has been expanded and refined. Two analytical plumes with known masses were run through the moment estimation procedure along with each of the 138 field plumes under analysis. One fictitious plume was placed in a sampler array