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

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Health and Environmental Sciences Department

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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.

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_{11}	152 [1]	3.15 [4]
p-Xylene	C_8H_{11}	156 [2]	3.15 [4]
m-Xylene	C_8H_{11}	146 [2]	3.20 [4]
o-Xylene	C_8H_{11}	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

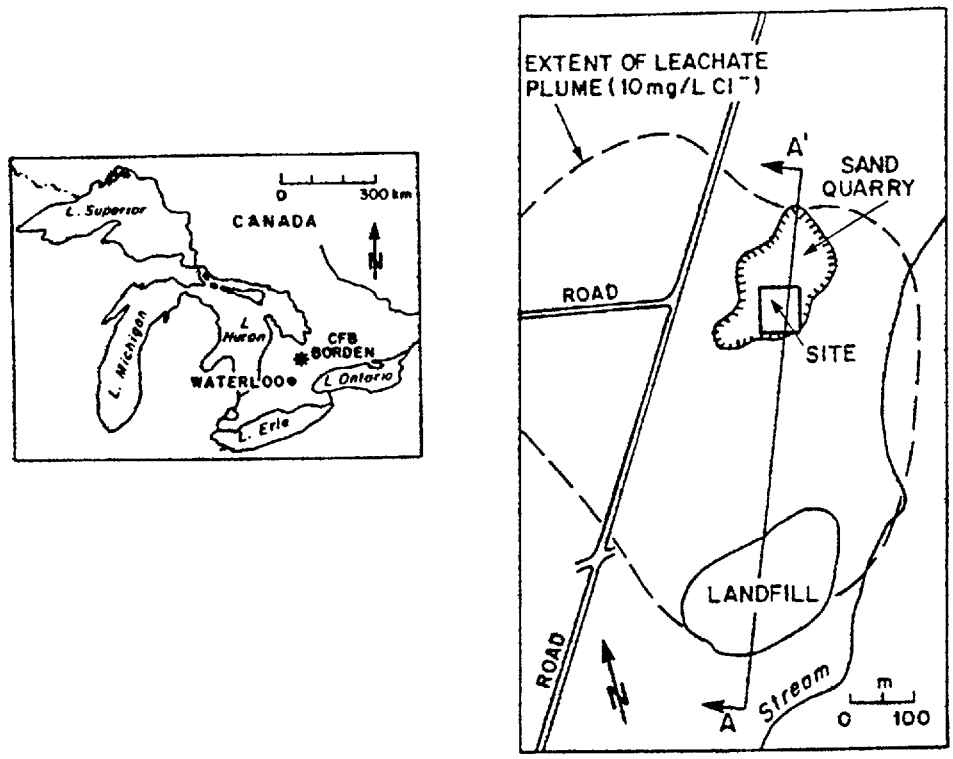
The natural gradient tracer test was conducted in a shallow, aerobic sand aquifer at Canadian Forces Base (CFB) Borden, Ontario. Pulses of groundwater contacted by each of the three fuels were simultaneously released below the water table. Chloride served as a conservative tracer. BTEX, oxygenate, and 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.



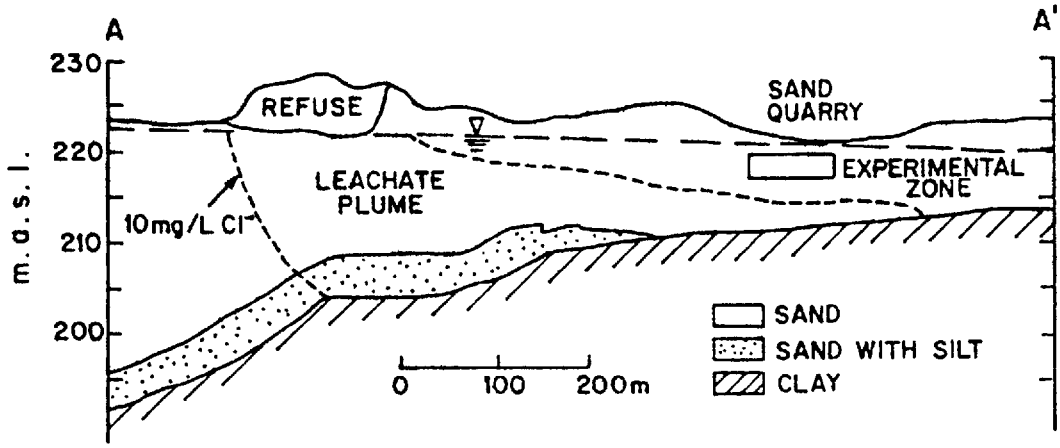


Figure 2-1. (a) Map of southern Ontario and the Great Lakes showing the location of CFB Borden; (b) Plan view of the test site in the Borden sand quarry showing the 1979 boundaries of the landfill leachate plume; (c) Site cross section showing the injection zone (after Mackay *et al.* 1986).

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/biomicrite 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
(2) Sudicky, 1986
(3) Mackay *et al.*, 1986
(4) Ball *et al.*, 1990
(5) Freyberg, 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.

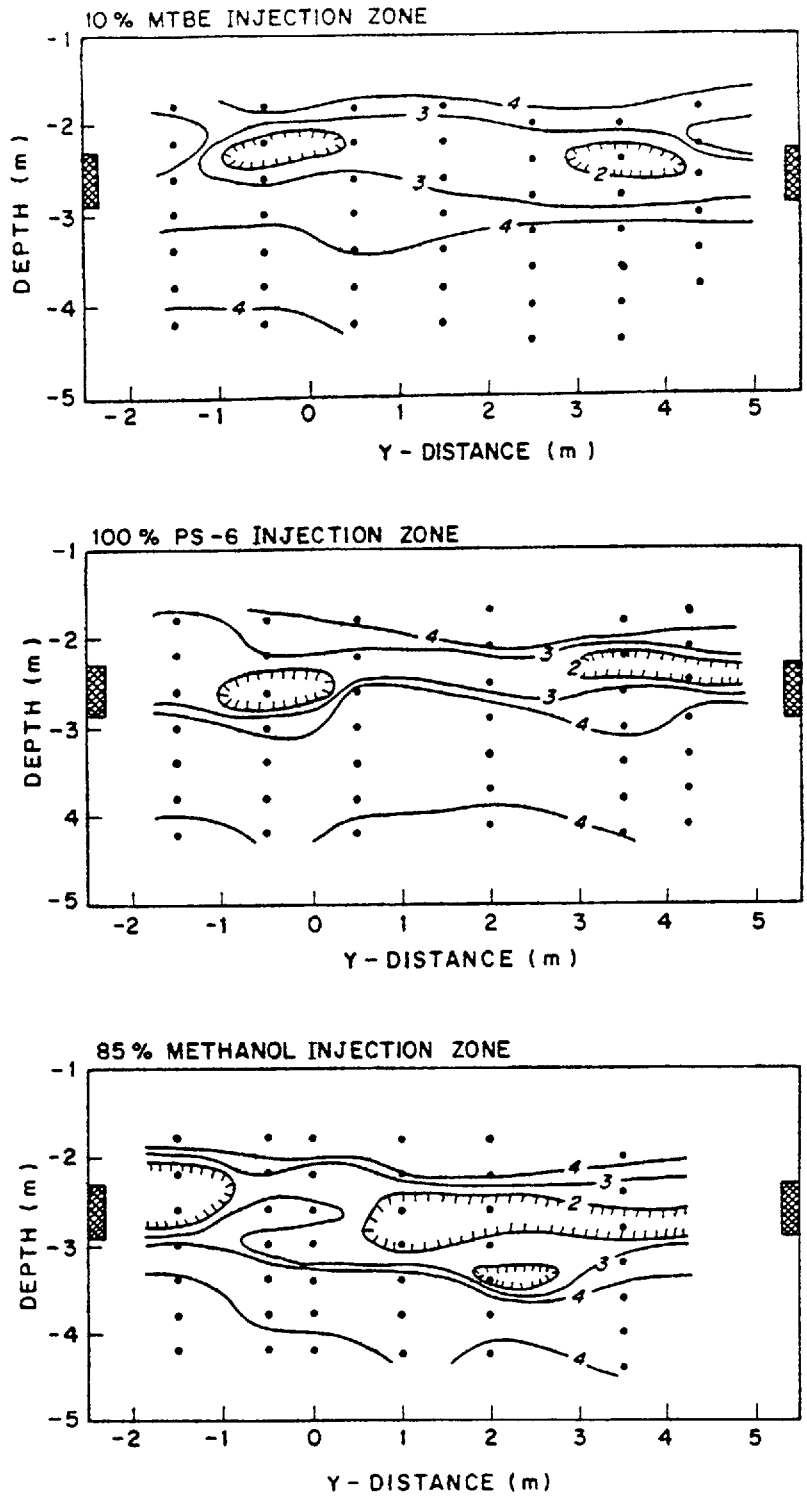


Figure 2-2. Longitudinal profiles of background dissolved oxygen distribution for the three injection zones. The injection interval is shown for reference.

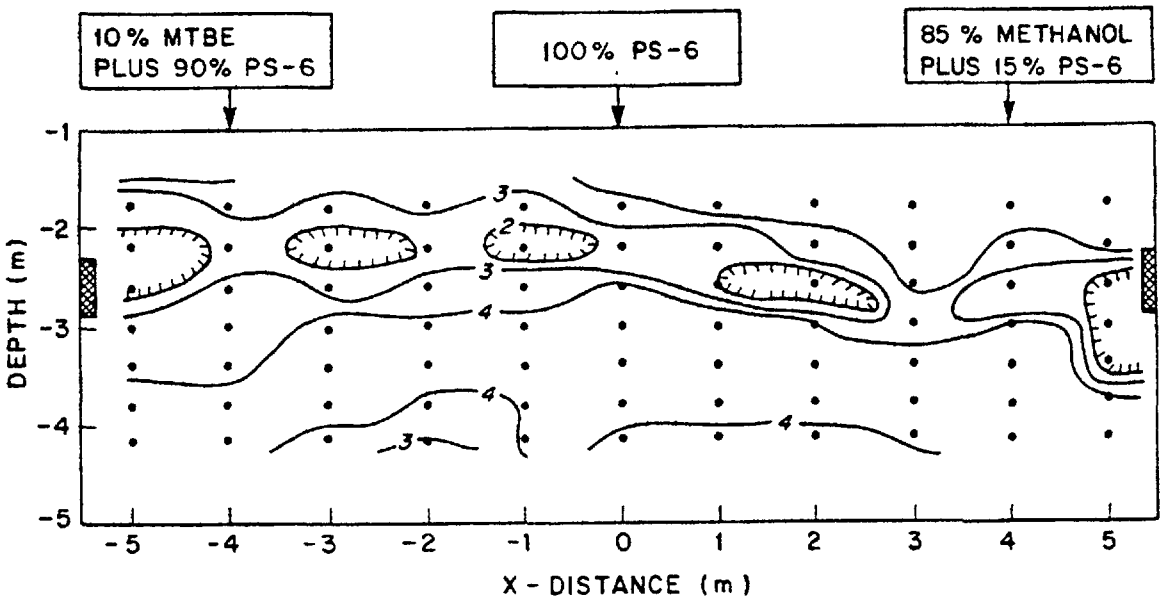


Figure 2-3. Transverse profile of background dissolved oxygen distribution at the three injection zones. The injection interval and points of injection are shown for reference.

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.

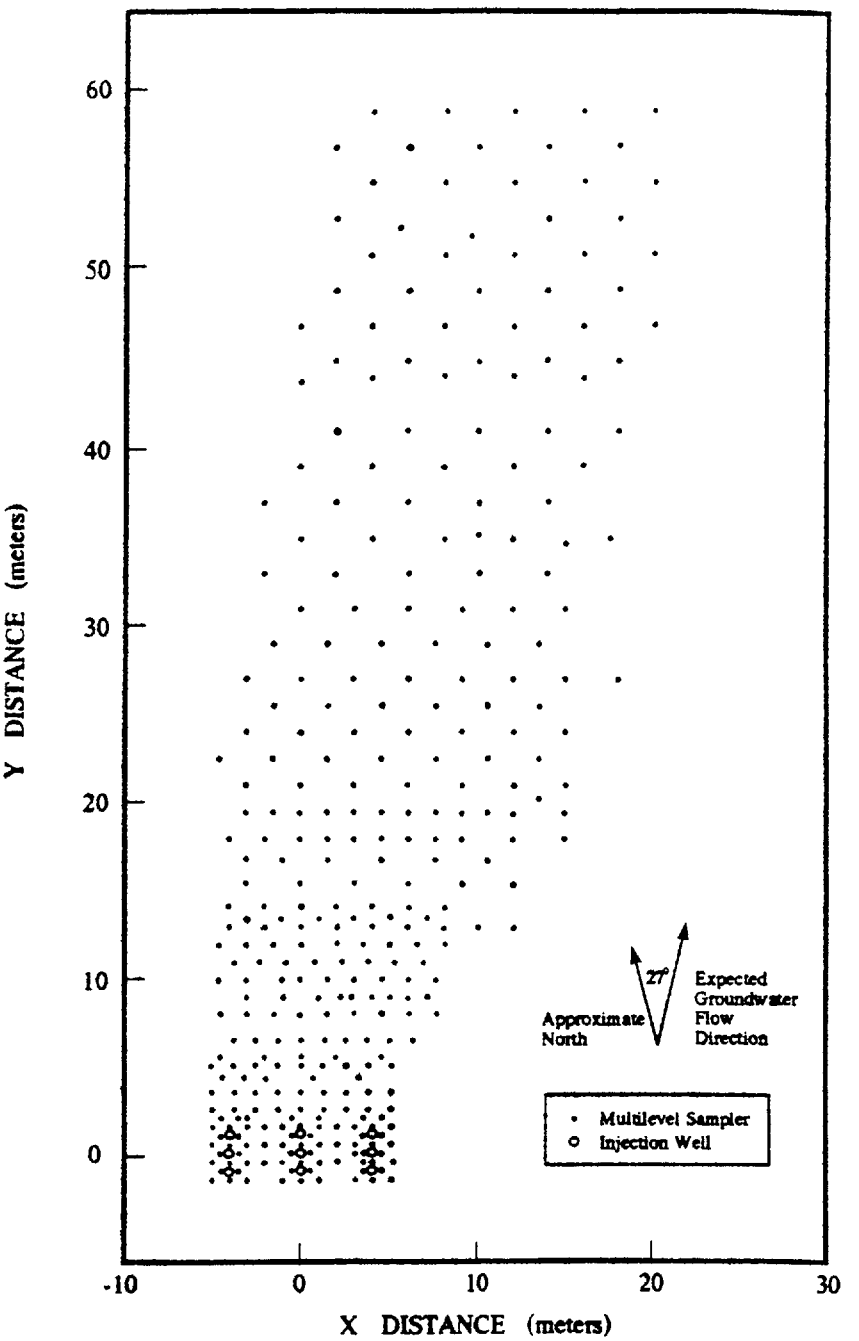


Figure 3-1. Plan view of the final array of multilevel samplers, and locations of the injection wells. The 10% MTBE pulse was injected on the left (1), the 100% PS-6 control pulse was injected in the center (2), and the 85% methanol pulse was injected on the right (3).

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:

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

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 griding 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

with a layout identical to the experimental monitoring network, while a second was placed in a regularly spaced sampler array. The analytical plumes were generated using a two-dimensional solution to the advection-dispersion equation for an instantaneous point source input to a uniform flow field (from Freeze and Cherry, 1979, eq. 9.6):

$$C(x,y,t) = \frac{M}{4\pi t\,(D_x\,D_y)^{1/2}}\, e^{\left[\frac{X^2}{4D_x t} - \frac{Y^2}{4D_y t}\right]}$$

where $C(x,y,t)$ = concentration at a given location for a given time (M/L^2)
t = time (T)
M = mass (M)
D_x, D_y = dispersion coefficients in the x and y directions (L^2/T)
X = x coordinate - vt (L), where v = average linear solute velocity (L/T)
Y = y coordinate

The equation can be solved for any location at any time using specified values for mass input and dispersion parameters. The shape of the analytically generated plumes was controlled by fixing the widths, and the fictitious plumes were rotated to match the orientation of the field plumes in the monitoring grid. A full explanation of the procedure for generating the fictitious plumes, and the FORTRAN code used for plume generation can be found in Skene (1991).

Estimated plume masses for the fictitious plumes were compared to the known masses to gain an understanding of two main sources of error: (1) the errors resulting from the positions of the samplers relative to the solute distribution (for example, insufficient sampler density at the plume core would produce an underestimation of mass), and (2) the estimation error due to the interpolation routine.

The combination of Surface II parameters that produced the smallest deviations in known mass for the fictitious plumes was used to run the field plumes through the areal interpolation routine. An explanation of the Surface II parameters chosen, and the rationale for the selections, is provided in Appendix E. Minimum errors in mass estimation for the fictitious plumes ranged from -13% to +41%, but the majority had

errors of -5% to +5%. The fewer the number of data points available per plume area, the greater the error observed, so the mass estimates for the mobile, biodegrading solutes at late times carry the least certainty. However, the masses for these plumes are small relative to the input mass, so a high percentage deviation of the estimated mass from the true mass is unlikely to alter overall interpretations of mass loss processes. Errors observed for a given time for each solute in each of the three test cases were generally comparable. A full evaluation of the quantitative relationship between errors observed for the fictitious plumes and the mass estimates for the field plumes has not been made, but the method was useful in parameter selection, and the data are available for further examination.

Section 5
OVERVIEW OF SOLUTE BEHAVIOR

This section presents qualitative observations of solute behavior based on depth integrated contour plots and longitudinal cross sections of the solute concentration distributions. Migration and fate of the organics are described with respect to the chloride tracer, and the three test cases are compared and contrasted. Transport and fate parameters are quantified in subsequent sections.

5.1 Areal Distributions of Solute Mass

Figures 5-1 through 5-6 show contour plots of the depth-integrated concentration data for selected solutes. The plots are representative of the areal distribution of solute mass. They are intended to illustrate the position and shape of the plumes, and to provide an overview of the mean behavior of the solutes.

Contour lines connect points of constant concentration. The concentrations corresponding to the contour lines shown in each figure are specified in the figure heading. In interpreting the contour plots, the outermost contour line encloses a region within which concentrations exceed the lowest concentration specified in the figure heading. The next contour line within this region encloses a region within which concentrations exceed the second lowest concentration specified in the figure heading, and so on.

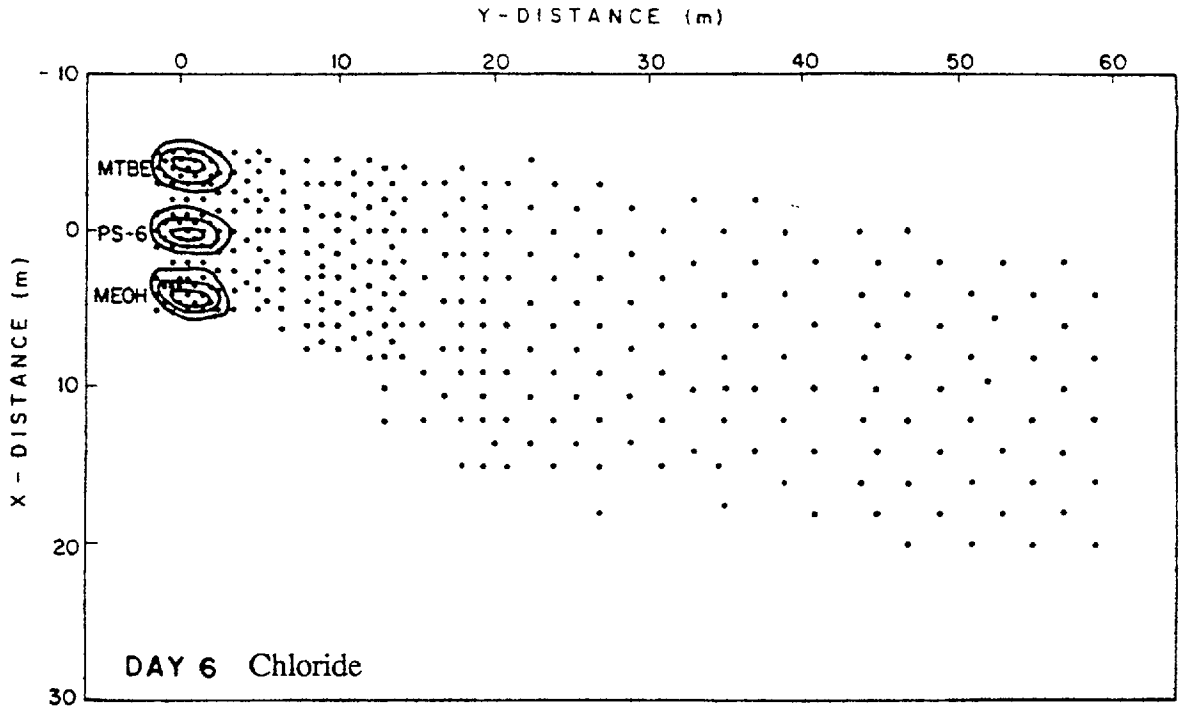
As an example, in the Day 6 contour plot of Figure 5-1, the chloride concentration in the region outside the outermost contour of each plume is less than 2 mg/L, and the chloride concentration within the region enclosed by the outermost contour exceeds 2 mg/L. The chloride concentration within the region enclosed by the next contour of each plume exceeds 100 mg/L, and the concentration within the region enclosed by the innermost contour of each plume exceeds 500 mg/L.

Chloride Tracers. Figure 5-1 shows chloride contour plots for four sample events. In general, chloride spread through time in the direction of groundwater flow. On Day 6, all three plumes were elliptical in plan view, with a length of five meters and a width of approximately three meters. By the final sampling round, after nearly sixteen months had passed, the plumes had expanded to a length of about 25 meters and a width of four meters. In all three cases, chloride exhibited substantial longitudinal dispersion, and very little lateral spreading.

The angle of the principal axis of the chloride plumes changed through time, shifting from an orientation parallel to the axis of the monitoring network to about 11 degrees east of the y axis of the network. Such a shift would have contributed to the lateral spreading of the chloride plumes. The final alignment of the plumes was essentially parallel to the expected flow direction.

In a previous tracer test at the site, a chloride plume developed a distinct bimodality during the first 85 days of transport (Mackay *et al.*, 1986). A plan-view bimodality of mass distribution was not observed for the chloride plumes of this experiment. However, on Day 317, there was an apparent breakup of the chloride plume in the 85% methanol case, as if a portion had stalled in a low velocity zone. At various times, the concentration distributions appeared to be skewed slightly forward or slightly backward, but there was no general trend in skew.

Minor lateral overlap of the plumes had occurred by Day 317, but they continued to be easy to distinguish from one another through the final sample round. The travel paths and degree of spreading were remarkably similar for the three plumes, indicating comparability of flow regime.



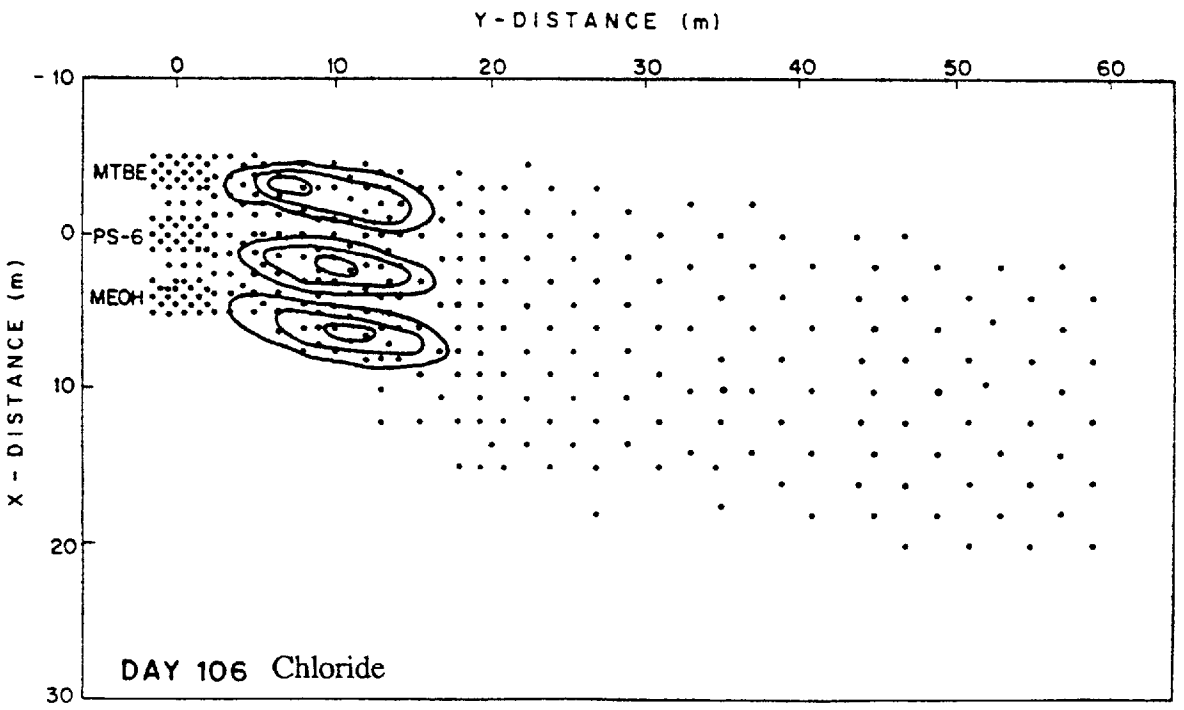
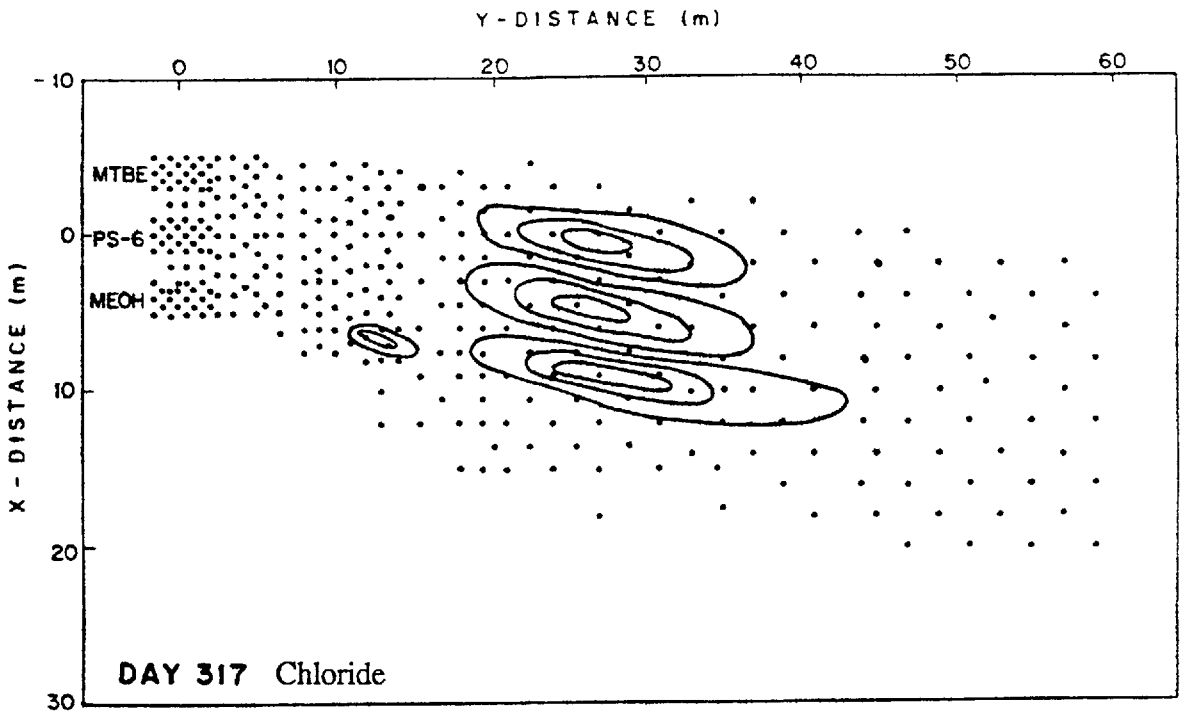


Figure 5-1. Contour plots of depth integrated chloride data for the first, third, fourth, and sixth sample rounds. Values of the contour lines are 2, 100, and 500 mg/L for Day 6 and 5, 100, and 300 mg/L for Day 106.



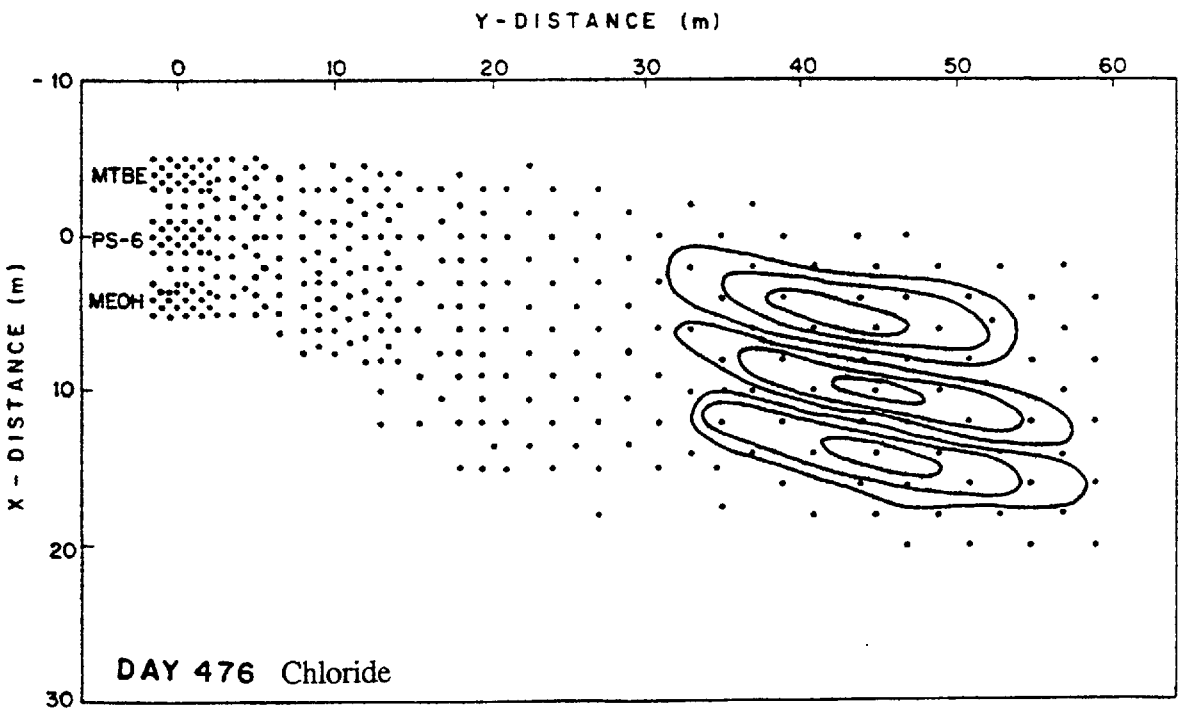


Figure 5-1. (continued) Values of the contour lines are 10, 50, and 100 mg/L for Day 317 and 10, 20, and 50 mg/L for Day 476.

Methanol and MTBE. Figure 5-2 shows contour plots of depth integrated data for the oxygenates. The initial mass distributions of the two oxygenates matched those of the chloride plumes. Through time, the MTBE maintained a mass distribution that corresponded to that of chloride, and it traveled at essentially the same rate. The methanol distribution was also nearly identical to that of the chloride through Day 106. However, by the fourth sample round, after about ten months of travel, the methanol plume was only three quarters of the length of the chloride plume. The mass distribution was skewed in the direction of flow, with a steeper gradient at the back and tailing toward the front. Since the chloride plume did not exhibit this skew, the change in mass distribution of methanol was probably not induced by transport phenomena. It is more likely that significant mass loss was occurring at the back of the methanol plume. By the final sampling round, nearly all of the methanol was reduced to concentrations below detection.

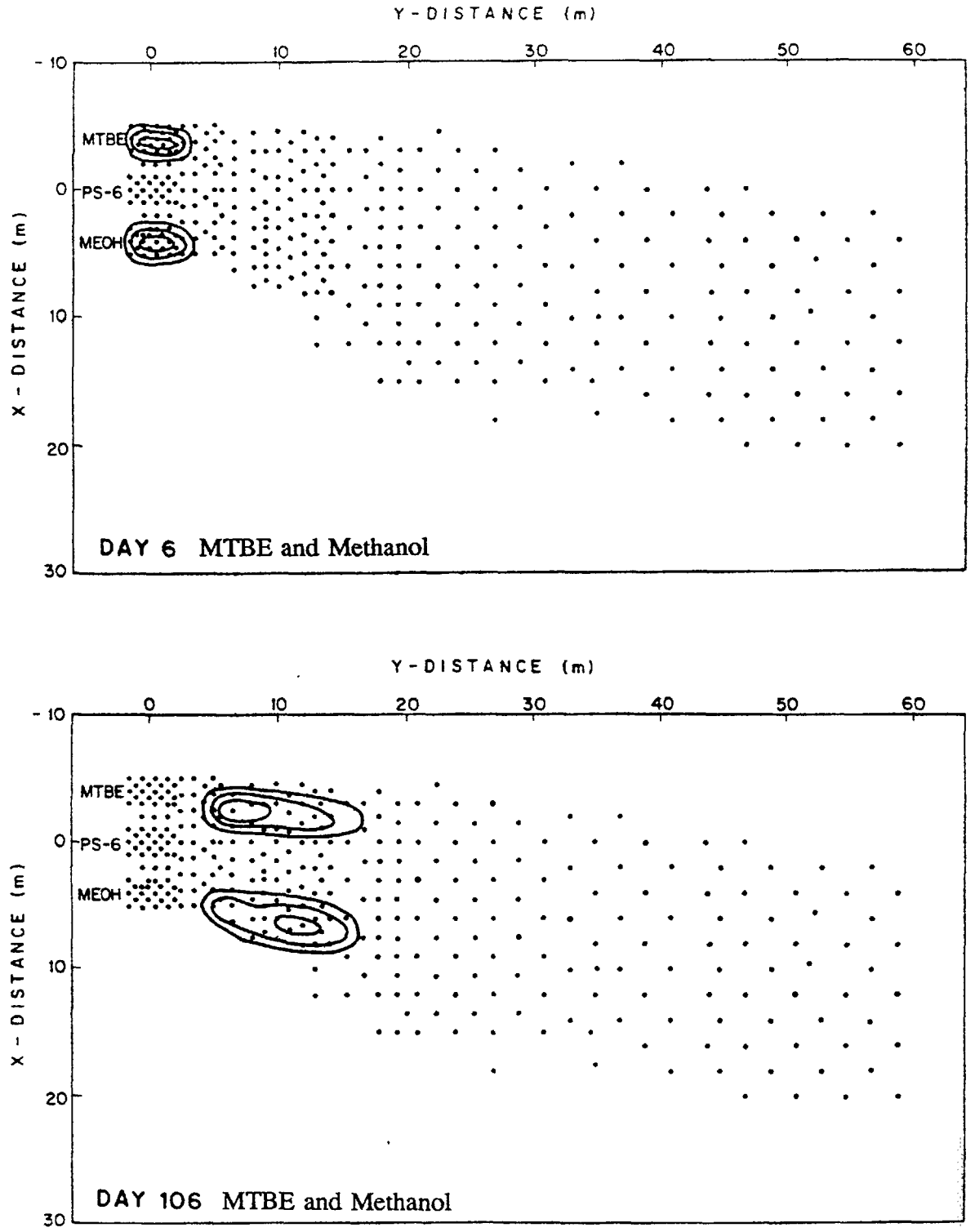
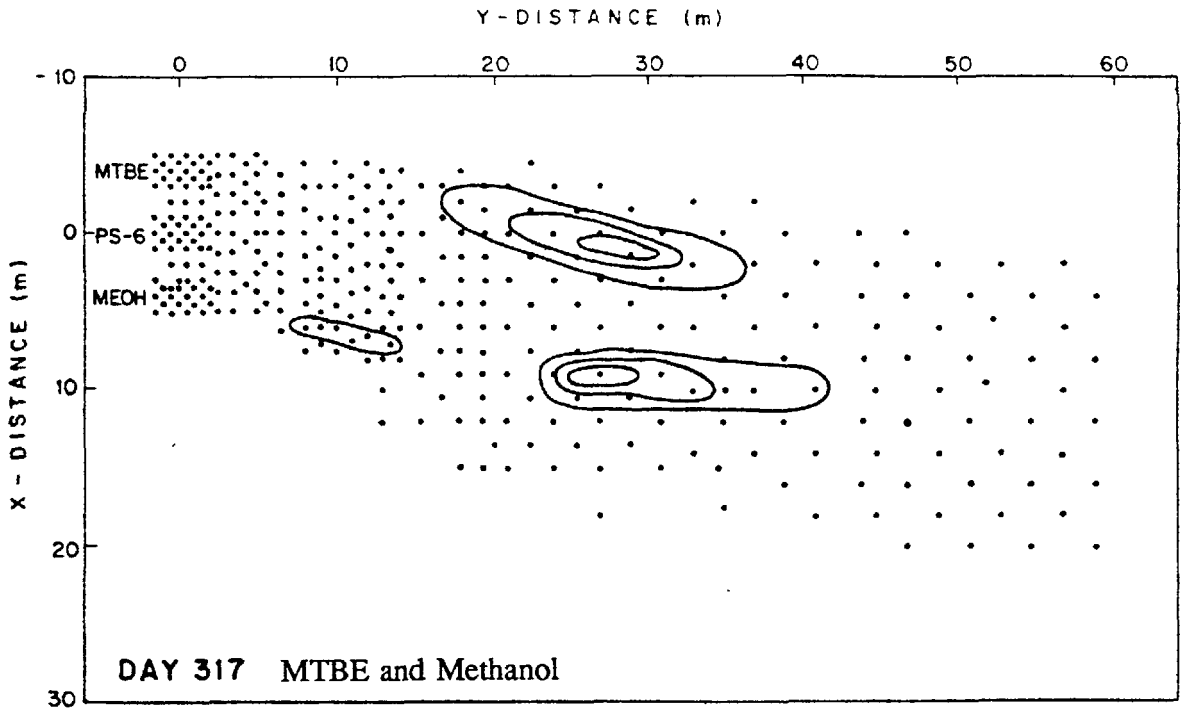


Figure 5-2. Contour plots of depth integrated methanol and MTBE data for the first, third, fourth, and sixth sample rounds. Values of the contour lines for MTBE are 1, 100, and 200 mg/L on Day 6 and 1, 20, and 100 mg/L on Day 106. Values of the contour lines for methanol are 1, 1,000 and 5,000 mg/L on Day 6 and 1, 100, and 5,000 mg/L on Day 106.



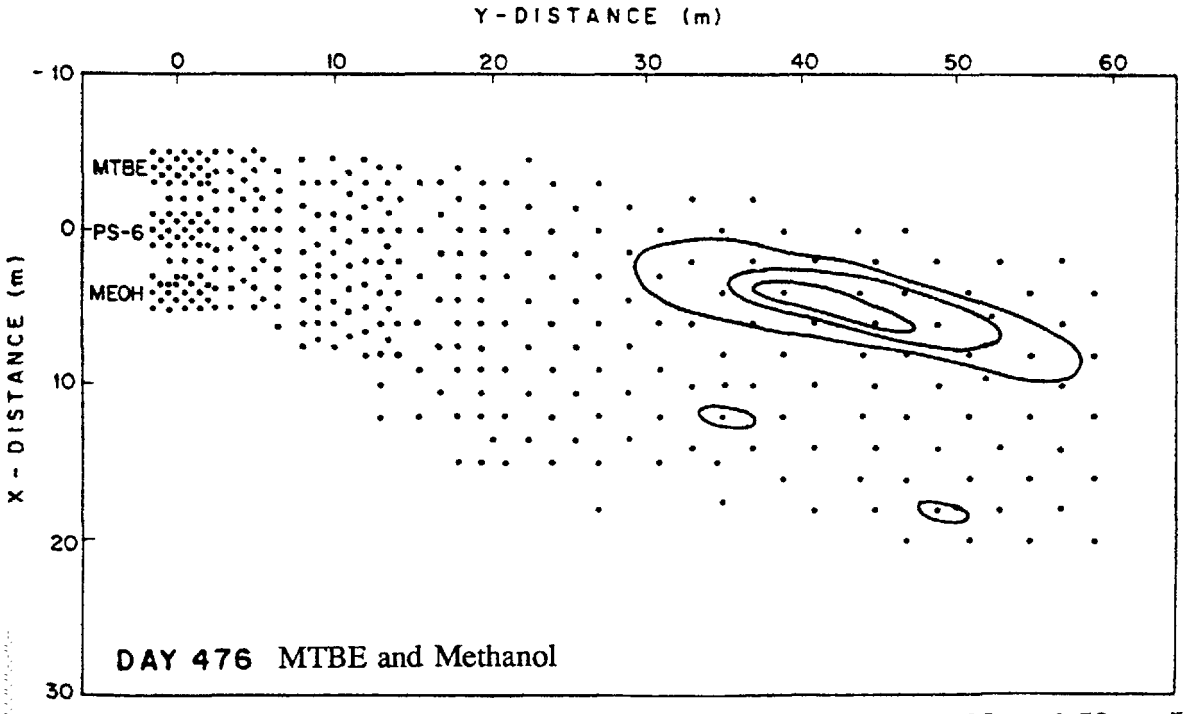


Figure 5-2. (continued) Values of the contour lines for MTBE are 1, 20, and 50 mg/L for both Day 317 and Day 476. Values of the contour lines for methanol are 1, 100, and 500 mg/L on Day 317 and 1 mg/L on Day 476.

Monoaromatic Hydrocarbons. All of the monoaromatic compounds had mass distributions that were similar to that of chloride as an initial condition. However, they migrated at different rates, according to their hydrophobicity. Through time, a chromatographic separation of the plumes occurred. The compounds showed varying degrees of longitudinal spreading depending on travel distance and amount of mass loss. The benzene plumes traveled the greatest distance and had the most longitudinal spreading. The other solutes spread less due to reductions in mass and shorter travel distances.

Figure 5-3 shows depth integrated contour plots for benzene. Through Day 106, the three benzene plumes were very similar in shape, elongating in the direction of groundwater flow. Beginning at Day 106, the mass distribution of the plumes was slightly skewed, with a tail of lower mass at the back. By Day 317, the tailing was pronounced in the control plume, and the benzene plume for the 85% methanol case was larger than that of the control. By the last sample round, the benzene plume for the 85% methanol case was clearly largest, and apparently contained significantly more mass than the other two cases.

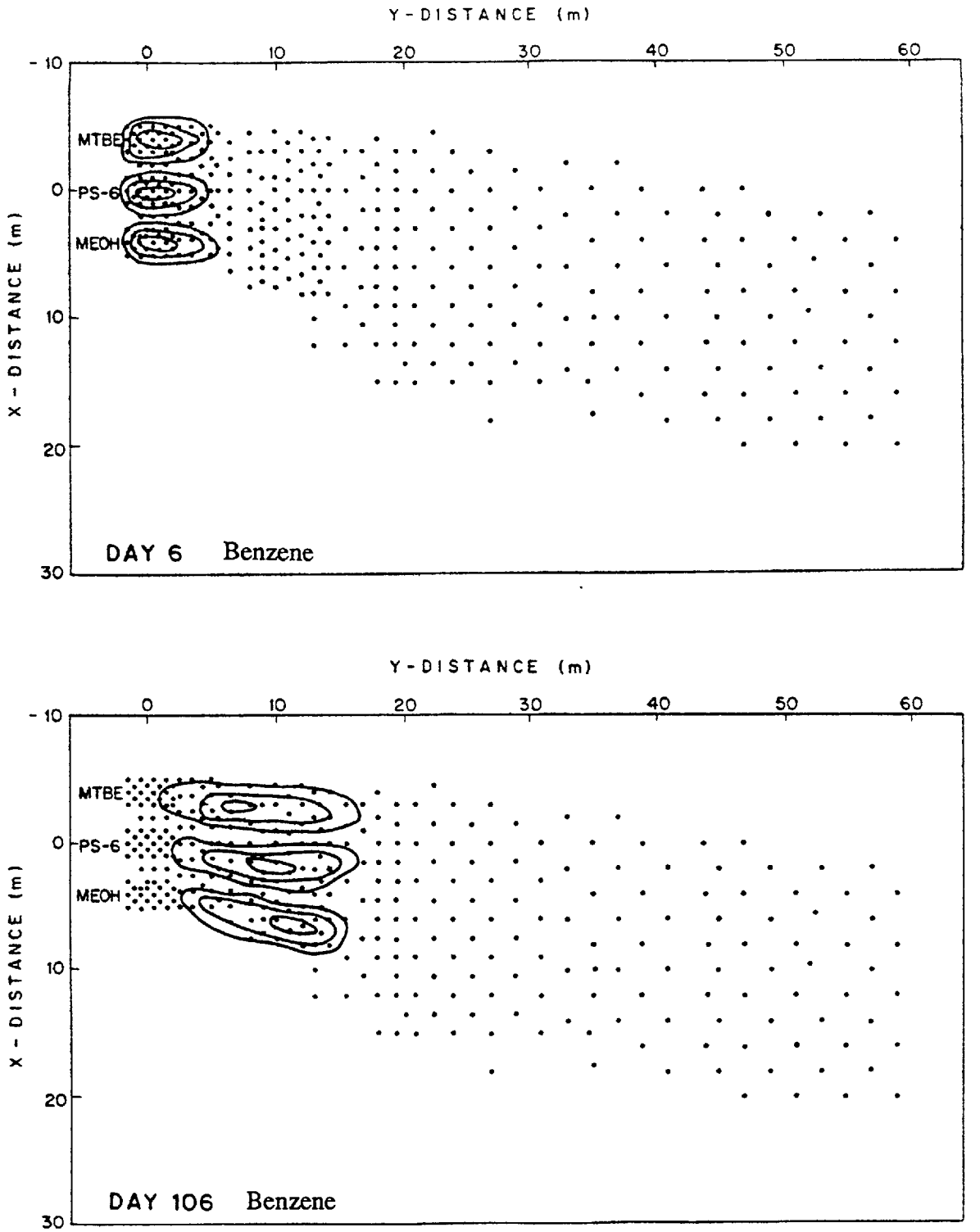


Figure 5-3. Contour plots of depth integrated benzene data for the first, third, fourth, and sixth sample rounds. Values of the contour lines are 1, 1,000, and 10,000 µg/L for Day 6 and 1, 1,000, and 5,000 µg/L for Day 106.

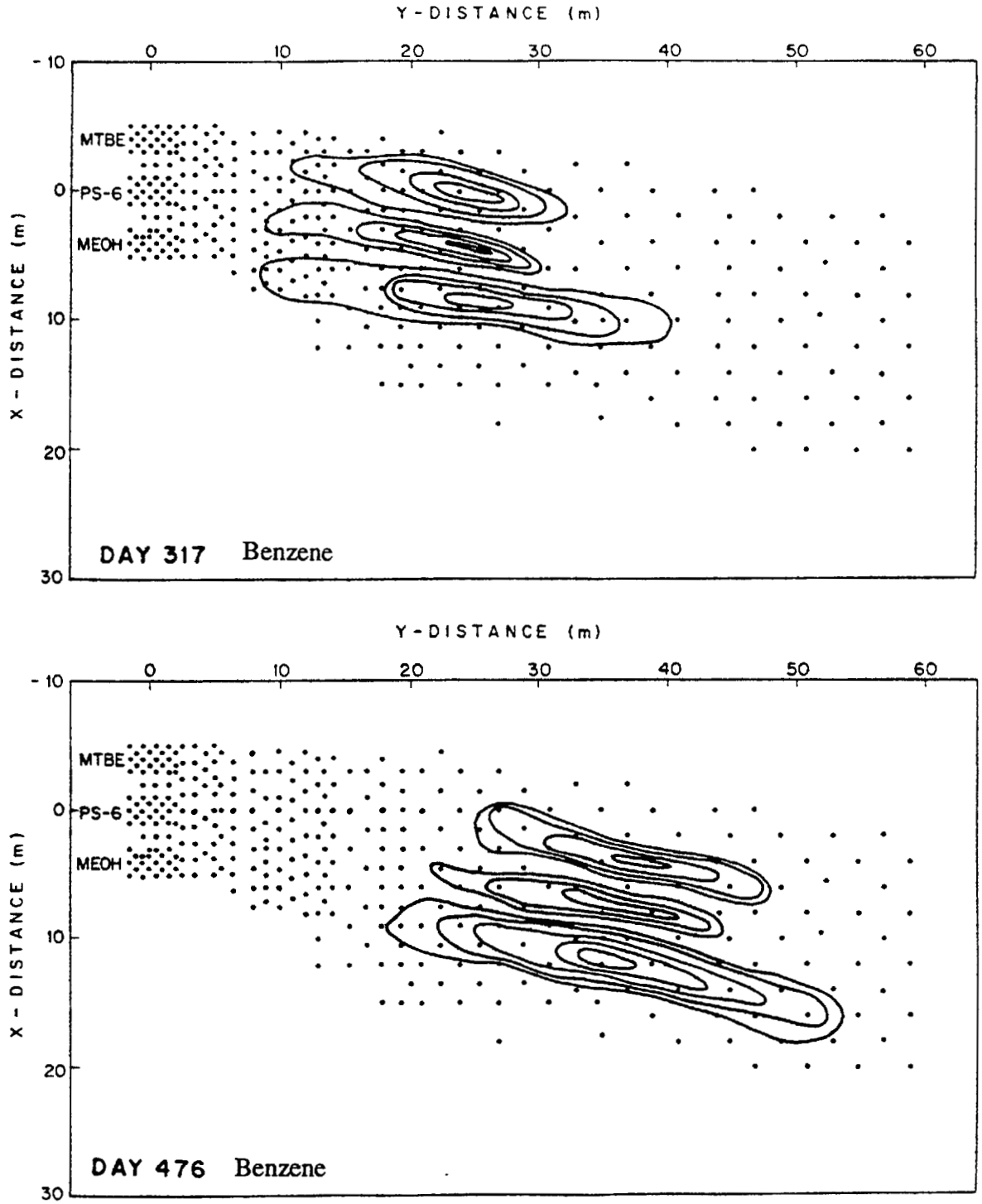


Figure 5-3. (continued) Values of the contour lines are 1, 100, 500, and 1,000 µg/L on Day 317. Values for the contour lines for Day 476 are 1, 50, 100, and 500 µg/L benzene for the 10% MTBE plume; 1, 50, and 100 µg/L benzene for the PS-6 plume; and 1, 50, 100, 500, and 1,000 µg/L benzene for the 85% MeOH plume.

Figure 5-4 depicts plan view mass distributions of toluene. All three toluene plumes lagged behind the benzene, and exhibited a slight tailing after the third sample round, with greater mass at the front end. By the fourth sample round, the plumes had a bimodal distribution, and they had narrowed in width relative to the initial condition. Peak depth-integrated concentrations had dropped dramatically. In sample rounds five and six, the plumes continued to shrink in length, although they essentially retained their widths. The tailing of the mass distribution, with the bulk of the mass at the front, was evident throughout the remainder of the experiment. The reductions in plume size with time suggest that in all three plumes significant toluene mass was lost. Dramatic differences among the three plumes were not apparent, although the toluene plume for the control case was smallest by the final sample round.

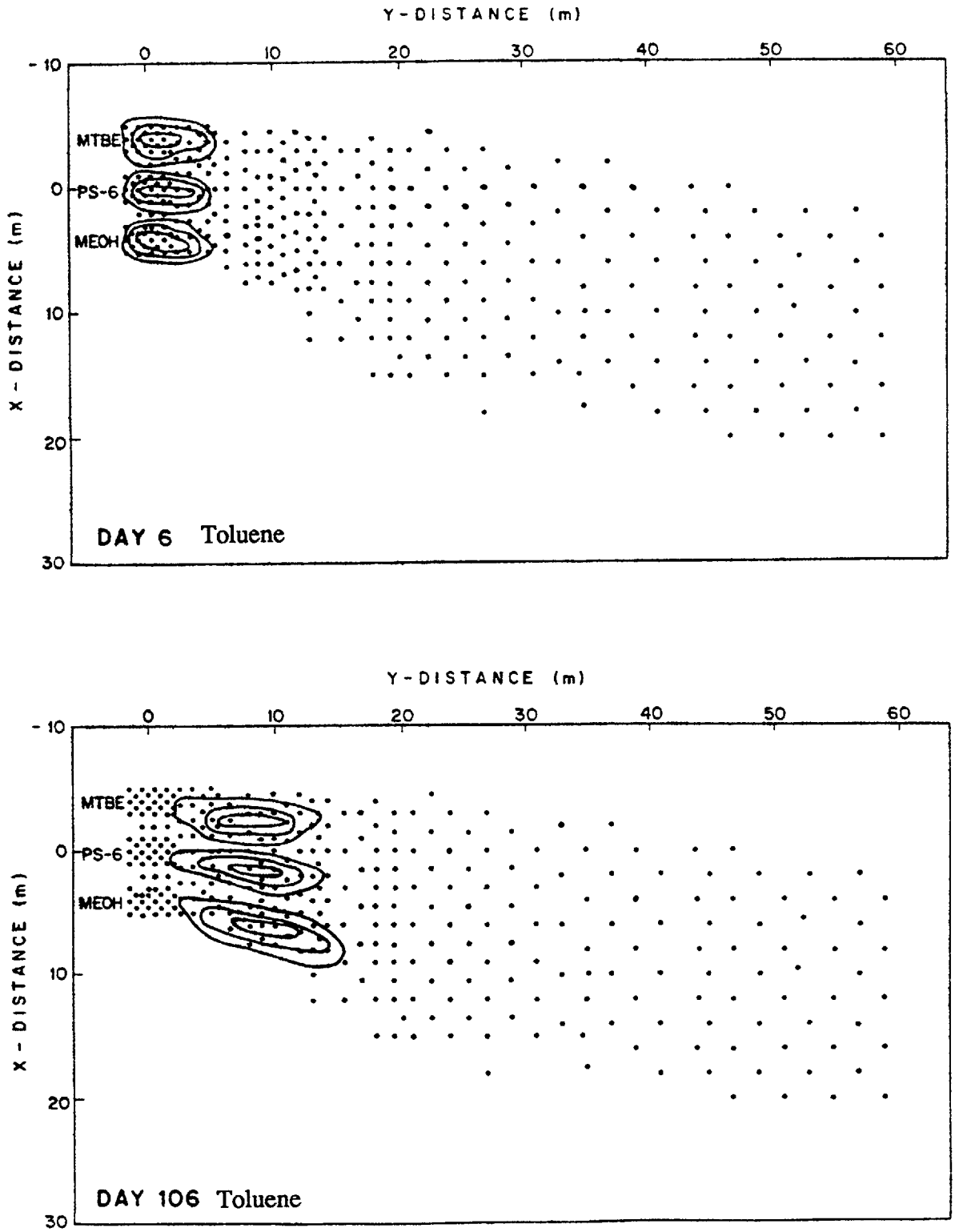


Figure 5-4. Contour plots of depth integrated toluene data for the first, third, fourth, and sixth sample rounds. Values of the contour lines are 1, 1,000, and 5,000 µg/L for Day 6 and 1, 500, and 1,000 µg/L for Day 106.

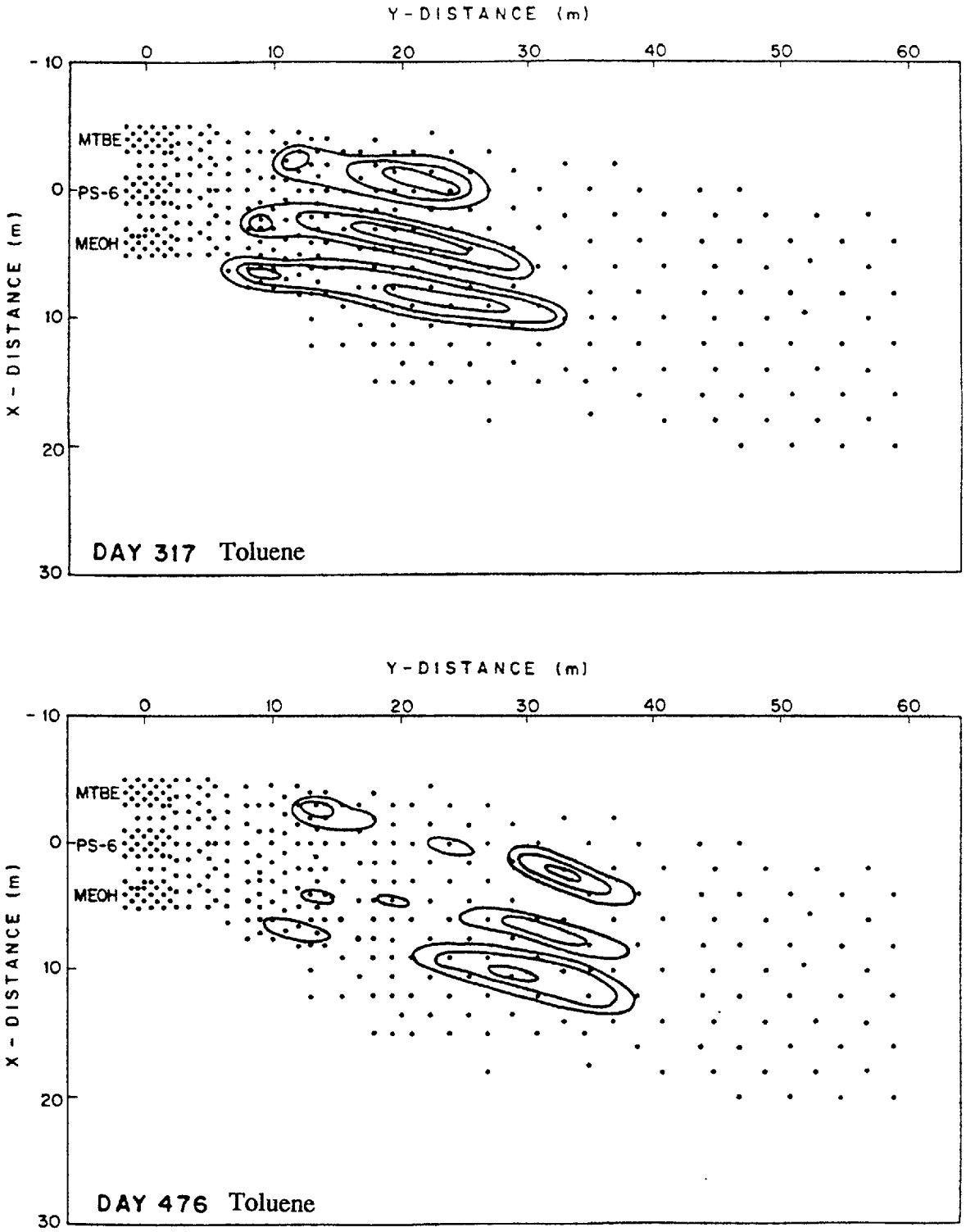


Figure 5-4. (continued) Values of the contour lines are 1, 10, and 100 µg/L for Day 317 and 1, 10, and 30 µg/L for Day 476.

Ethylbenzene, p-xylene, and o-xylene distributions were very similar to one another during the entire experiment. As an example of their migration, Figure 5-5 depicts contour plots of depth-integrated p-xylene concentrations. All three solutes traveled well behind toluene, essentially in tandem. By Day 106, a slight skew of the mass distributions was apparent: the bulk of the mass of each plume resided at the back. All were consistently shorter and narrower than the chloride plumes following the first sample round, exhibiting reduced dispersion due to the combined effects of shorter travel distances and loss of mass.

By the fourth sample round, differences were apparent among the three cases. Ethylbenzene, p-xylene, and o-xylene plumes of the 85% methanol case appeared larger and had greater values of peak depth integrated concentration than the control case. By the fifth and sixth sample rounds, some of the plumes for the 10% MTBE and 100% PS-6 cases had broken into two sections, while all of those for the 85% methanol case remained intact. m-Xylene traveled at the same rate as the two other xylene isomers and ethylbenzene, but it lost mass much more rapidly. The m-xylene was detectable in only a few points by the final sample round (Figure 5-6).

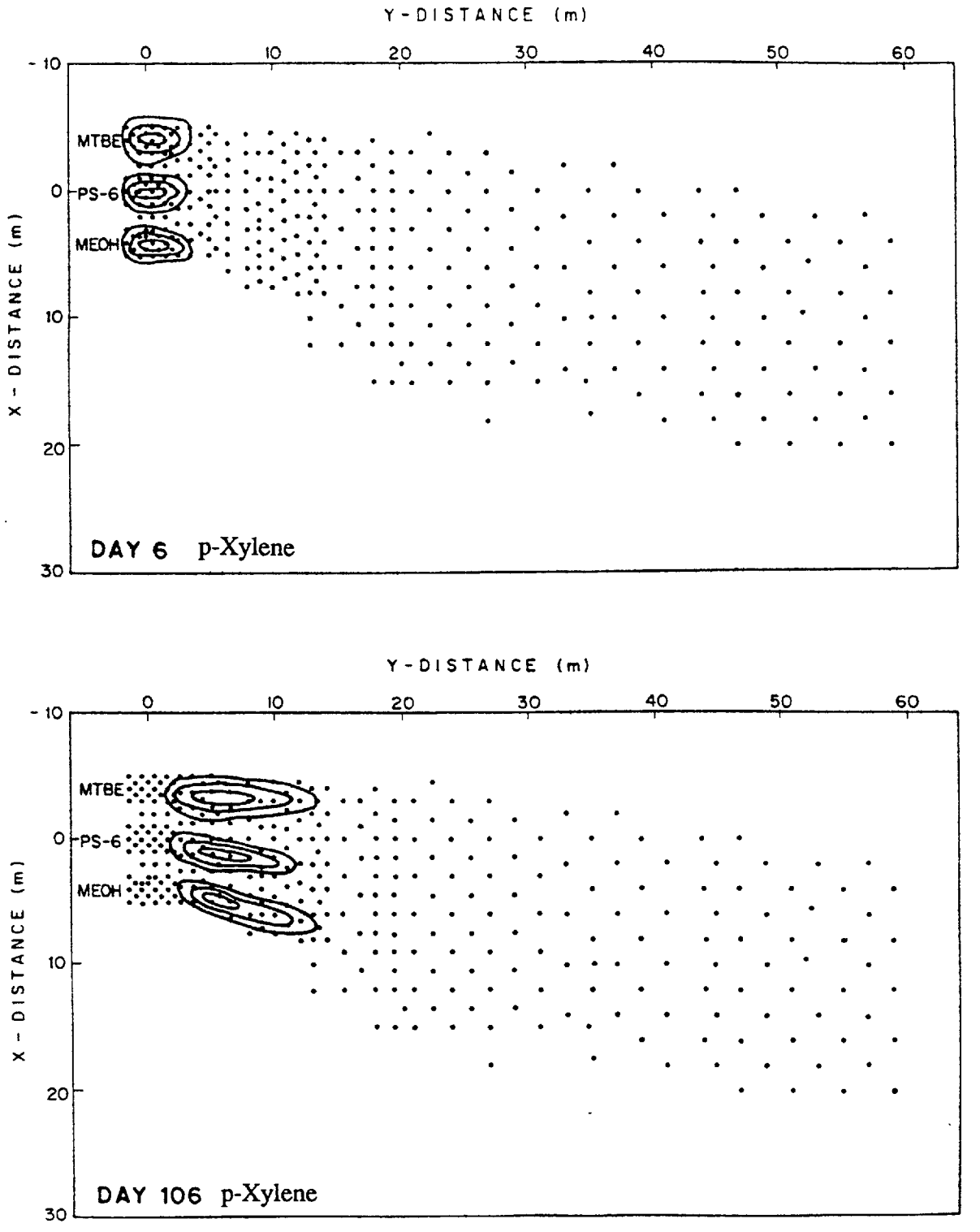


Figure 5-5. Contour plots of depth integrated p-xylene data for the first, third, fourth, and sixth sample rounds. Values of the contour lines are 1, 100, and 1,000 µg/L for Day 6 and 1, 100, and 300 µg/L for Day 106.

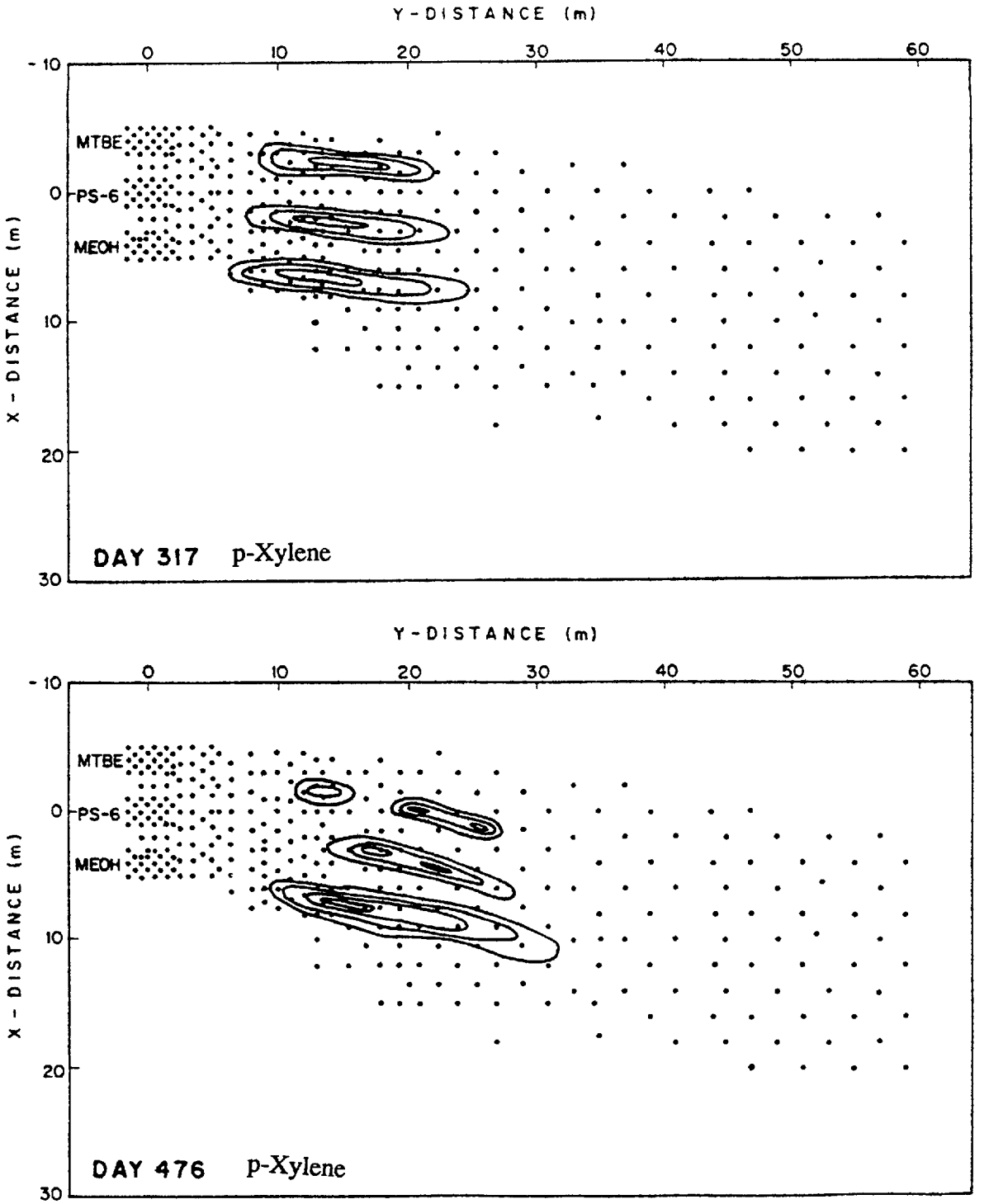


Figure 5-5. (continued) Values of the contour lines are 1, 20, and 100 µg/L for Day 317. Values of the contour lines for Day 476 are 1, 20 and 40 µg/L p-xylene for the 10% MTBE plume; 1, 20 and 40 µg/L p-xylene for the PS-6 plume; and 1, 20, 40, and 100 µg/L p-xylene for the MeOH plume.

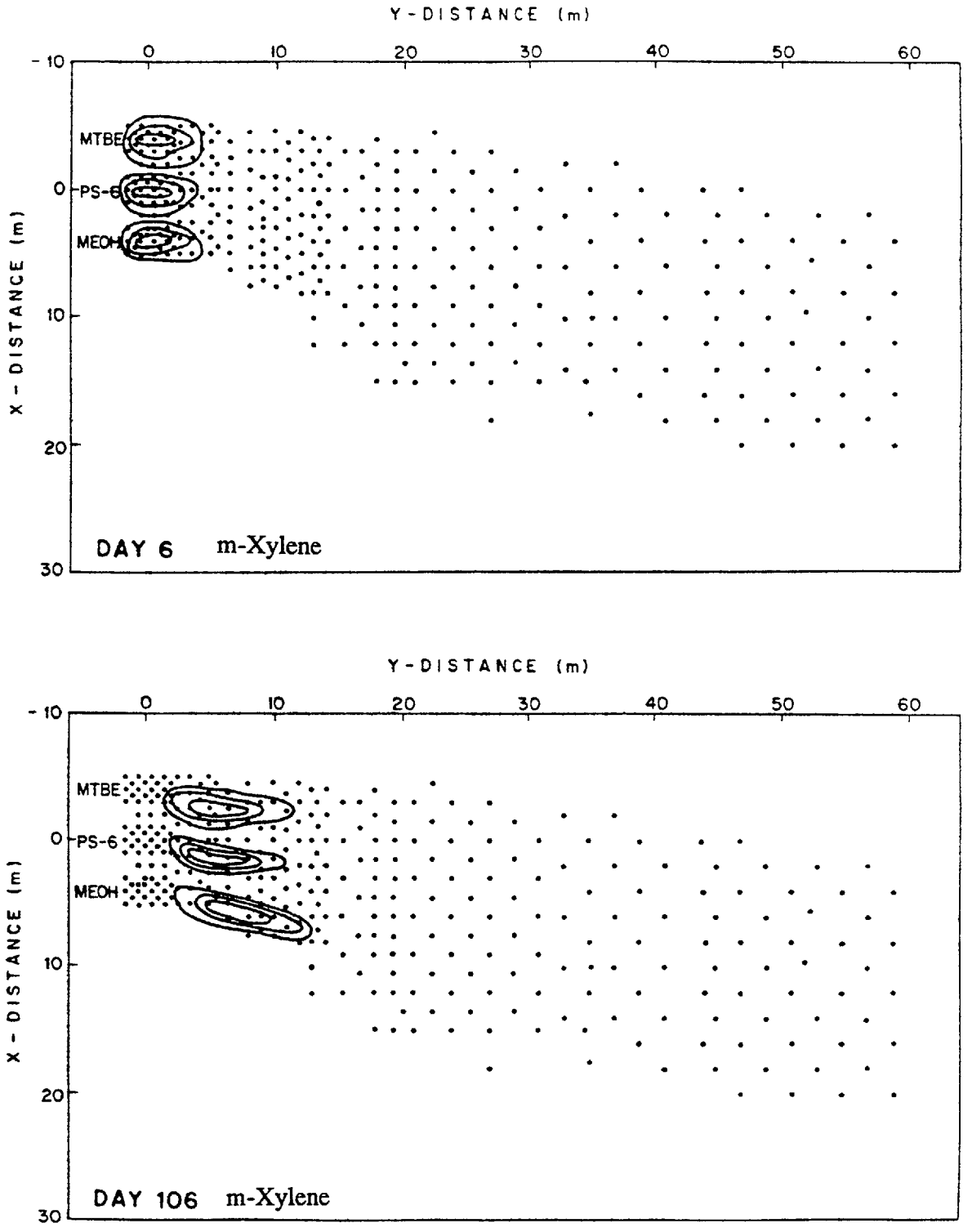


Figure 5-6. Contour plots of depth integrated m-xylene data for the first, third, fourth, and sixth sample rounds. Values of the contour lines are 1, 100 and 1,000 µg/L for Day 6 and 1, 100, and 500 for Day 106.

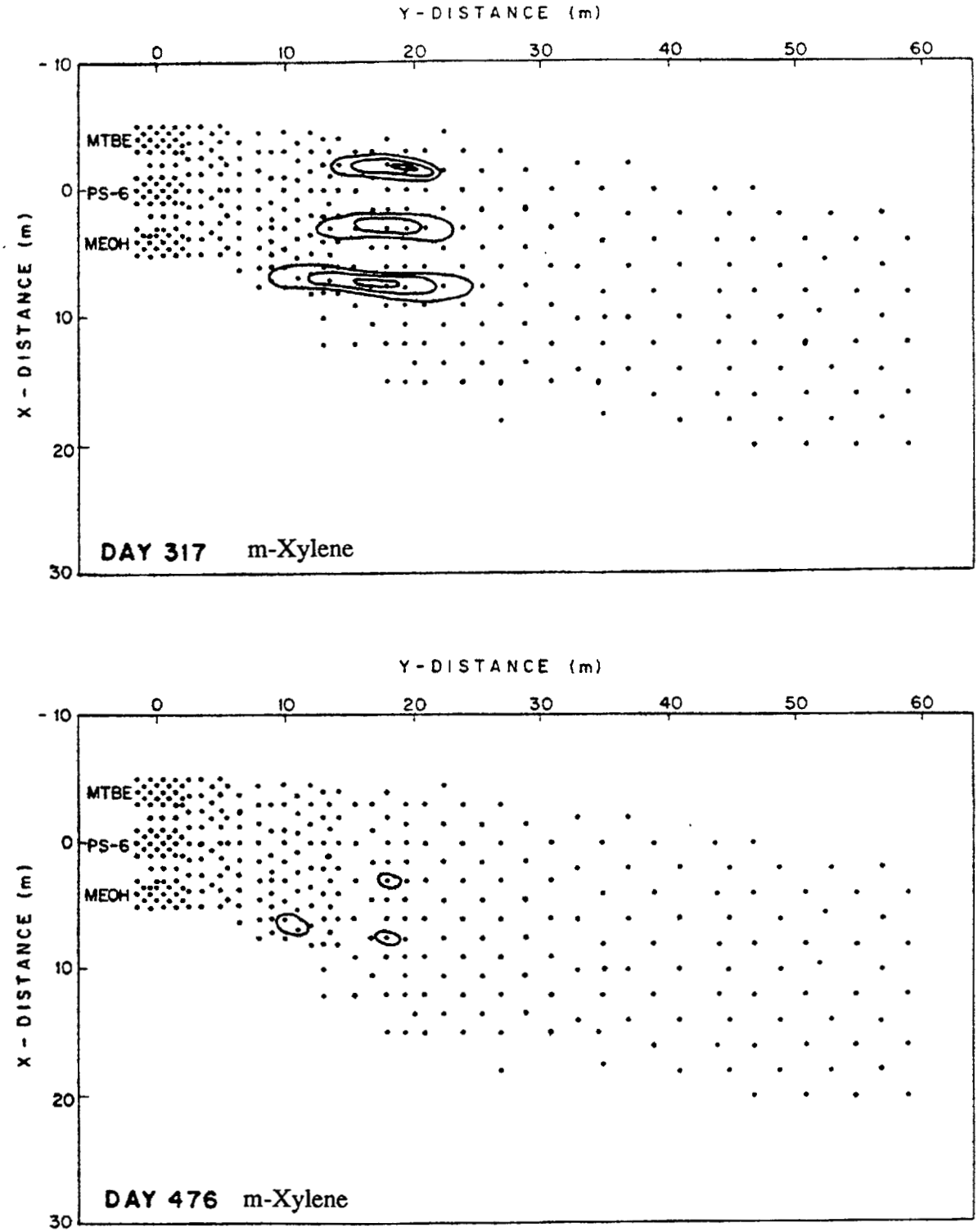


Figure 5-6. (continued) Values of the contour lines are 1, 50, and 100 µg/L for Day 317 and 1 µg/L for Day 476.

5.2 Vertical Solute Concentration Distributions

This section presents general observations of the changes in plume thickness and vertical concentration distribution with time for the conservative and reactive solutes. Figures 5-7 through 5-10 are contour plots of the solute concentration distributions along the plume centerlines. A key to the piezometers selected for each Figure is provided in Appendix F.

Chloride Tracers. The chloride pulses were approximately 1.5 meters thick at the first sampling event. Vertical concentration gradients were very steep: concentrations dropped from about 500 mg/L to background levels (2 mg/L) within 20 cm at the top and base of the plumes. Over time a bimodal concentration distribution developed. There was a distinct upper zone in which chloride was transported more rapidly and a lower zone in which chloride transport was slower. Each zone was about a meter thick. Areas of high chloride concentration in each lobe were offset by a couple of meters.

Figure 5-7 shows longitudinal cross sections of the chloride plumes of the 85% methanol case on Days 106 and 476. They closely resemble those of the control and 10% MTBE cases, and are intended to illustrate processes occurring in all three. As shown in the Figure, the bimodal distribution was very distinct on Day 106: in a narrow (<20 cm) zone between the lobes, chloride concentrations were indistinguishable from background.

By the final sample round, the vertical and horizontal concentration gradients were much less steep, and an overall smoothing of the concentration distribution was evident. Although the bimodal distribution persisted to some degree, the upper and lower portions of the plumes merged. The upper zone did not move enough beyond the lower zone to make the mass distributions appear bimodal in plan view, but such a bimodality could develop with time. The existence of the zones would tend to increase longitudinal spreading of the plumes relative to a system with a more homogeneous velocity distribution.

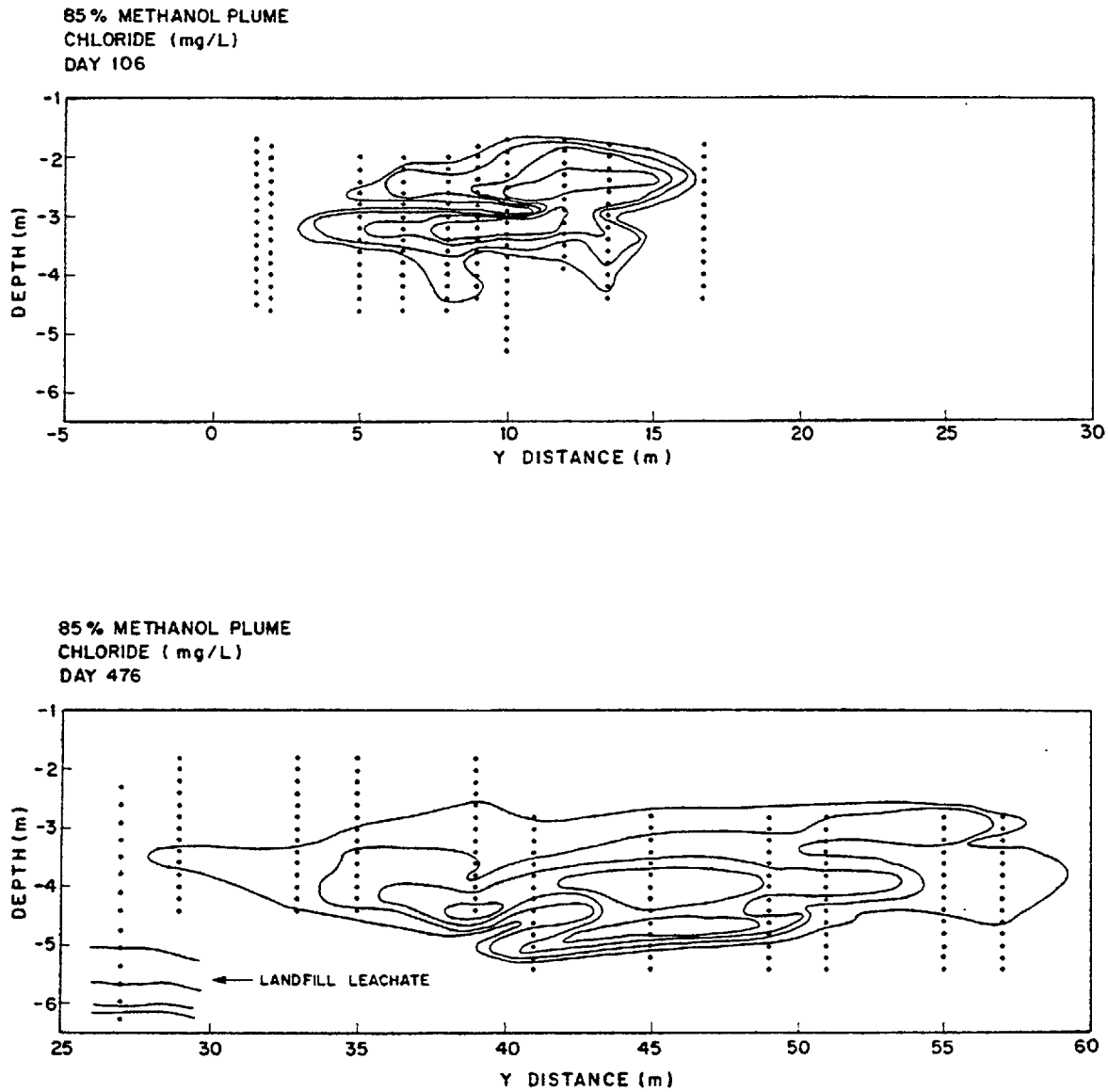


Figure 5-7. Profiles of chloride concentration along the centerline of the 85% methanol plume on Day 106 and Day 476. Values of the contour lines are 2, 10, 100 and 300 mg/L for Day 106; and 2, 10, 30, and 50 mg/L for Day 476.

Methanol and MTBE. The concentration distribution for MTBE (not shown) closely matched that of the chloride tracer through the final sampling round. The methanol distribution also matched that of chloride through Day 106, but the methanol plume subsequently began to shrink dramatically. Figure 5-8 shows the methanol and chloride distributions in the 85% methanol case on Day 317. By this sample event, a five-meter back section of the methanol plume had been reduced to concentrations below detection, and concentration gradients in the remainder of the plume were higher than in the chloride plume. By the fifth sample round (not shown), the methanol persisted in only a few "hotspots" at 40 mg/L. The hot spots were 0.6 m thick (one third of original plume thickness) and less than one fifth of the length of the chloride plume. Their scale was similar to that of the aquifer bedding. By the final sample event, there were only two occurrences of methanol, each about 10 mg/L, separated by distances up to 25 m.

Monoaromatic Hydrocarbons. Vertical solute distributions for the monoaromatic hydrocarbons were highly correlated with that of chloride at the first sample round. However, with time, the concentration gradients at the plume margins became steeper for the monoaromatics than for the conservative tracer. The sharpest concentration gradients existed at the leading edges of the BTEX plumes. As an example, Figure 5-8 shows the benzene distribution for the 85% methanol case on Day 317 and the chloride plume on the same day. The complexity of the solute distributions for the monoaromatics also increased with time, as illustrated in Figure 5-9, which shows the toluene distribution in the 85% methanol plume for the third and fifth sample rounds. The effect was most pronounced for plumes with a rapidly diminishing mass. In addition, the thickness of the BTEX plumes tended to decrease with time, especially for the less mobile solutes. As an example of this phenomenon, Figure 5-10 shows the p-xylene distribution in the 85% methanol plume on Day 398 and Day 476. The thinning was the most pronounced for these later sample events. As shown in both Figures 5-9 and 5-10, the monoaromatics tended to persist in discreet lens-shaped zones that had scales similar to the structural bedding of the aquifer. By the final sample rounds, several of the solute plumes were composed of unconnected solute lenses.

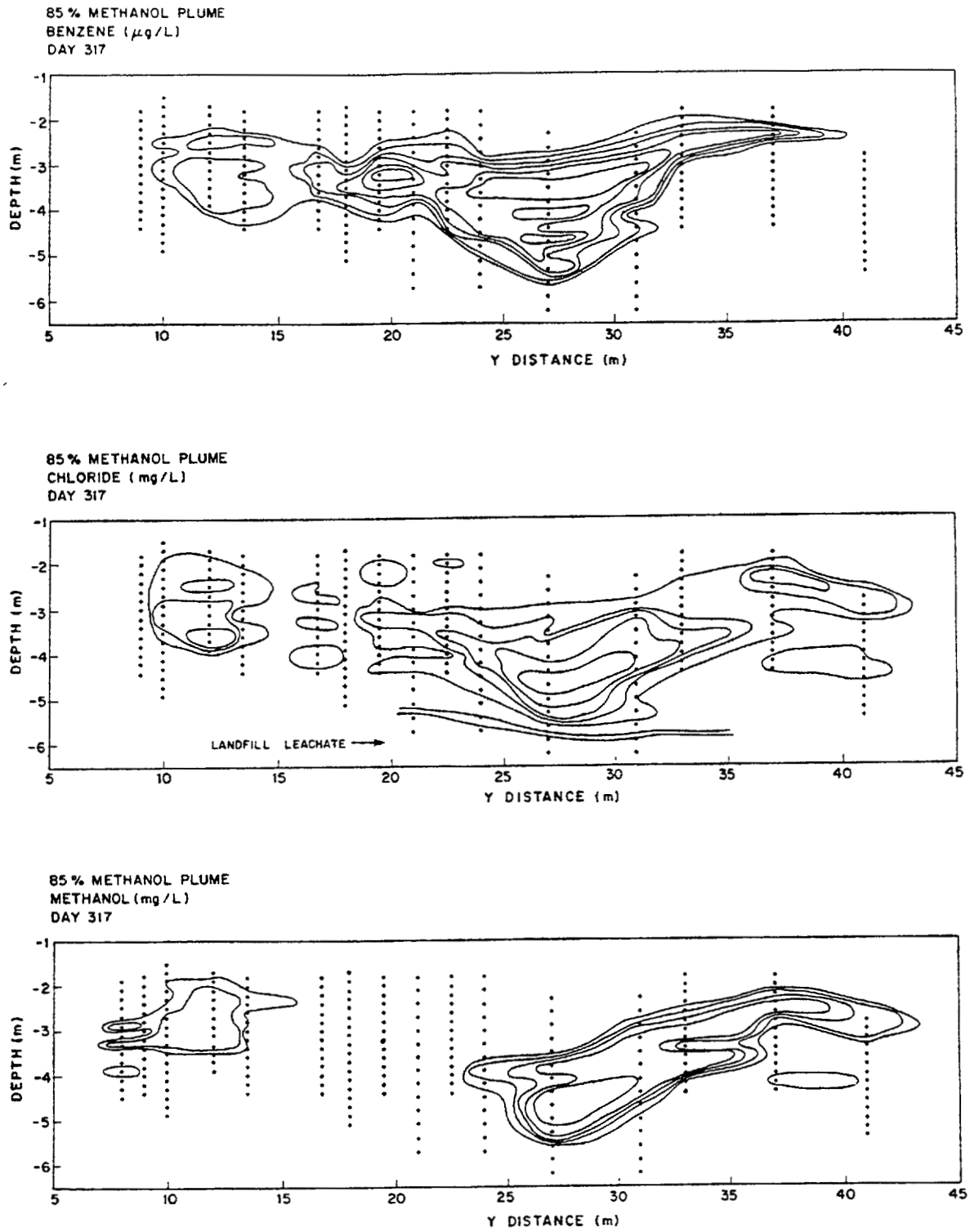


Figure 5-8. Profiles of benzene, chloride, and methanol concentration along the centerline of the 85% methanol plume on Day 317. Values of the contour lines for benzene are 1, 10, 50, 100, 500, and 1,000 µg/L, for chloride are 2, 10, 50, 100 and 200 mg/L; and for methanol are 1, 10, 50, 100, and 500 mg/L.

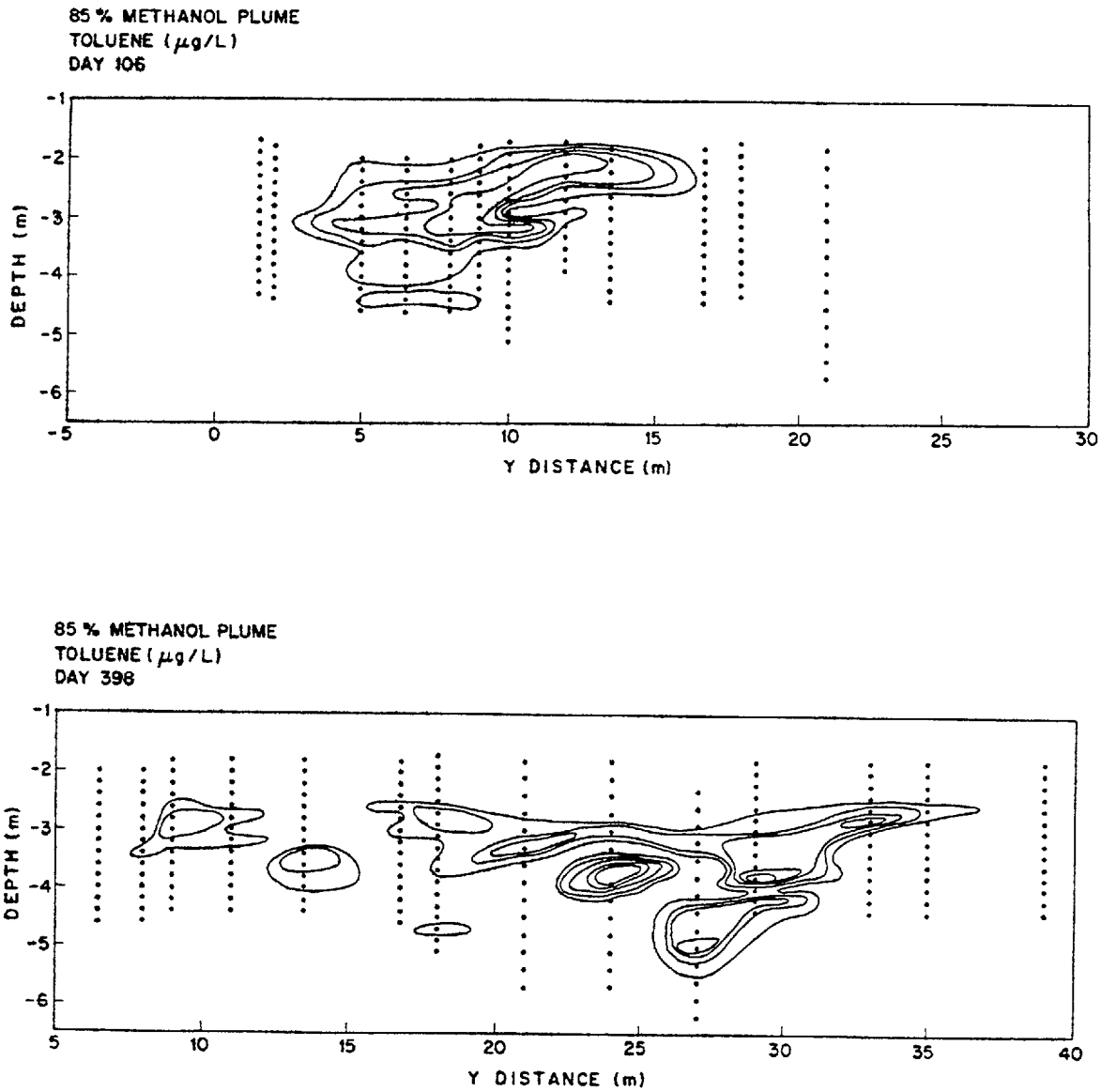
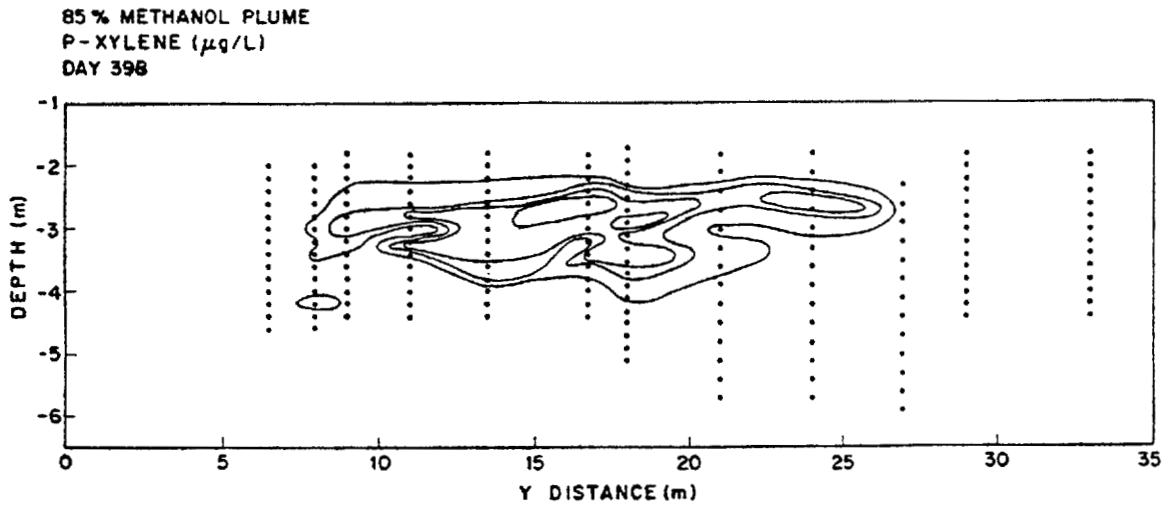


Figure 5-9. Profiles of toluene concentration along the centerline of the 85% methanol plume on Day 106 and Day 398. Values of the contour lines for are 1, 100, 1,000 and 3,000 µg/L for Day 106 and 1, 10, 20, and 50 µg/L for Day 476.



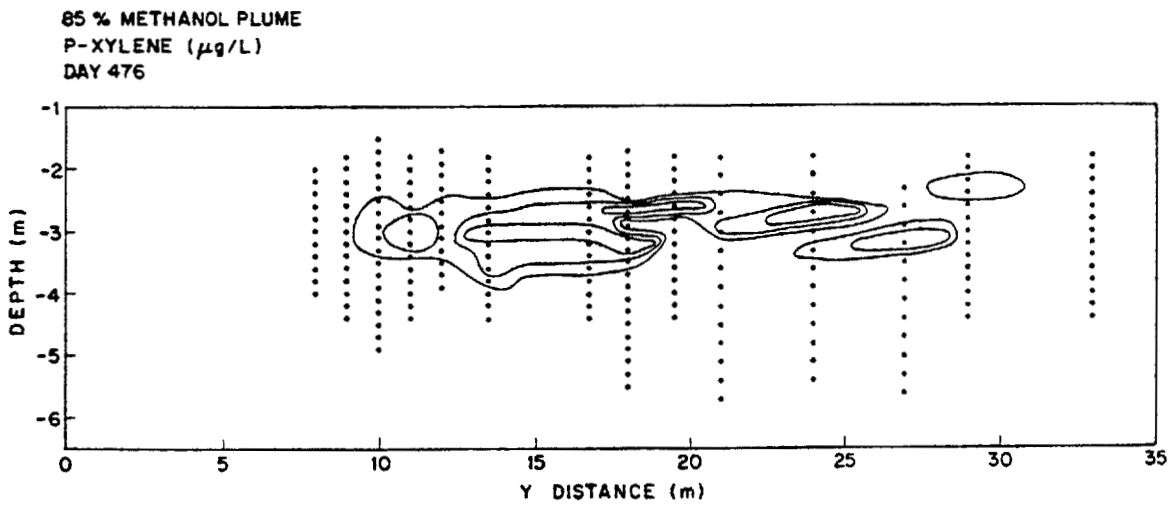


Figure 5-10. Profiles of p-xylene concentration along the centerline of 85% methanol plume on Day 398 and Day 476. Values of the contour lines are 1, 20, 50 and 100 µg/L for Day 398, and 1, 20, and 50 µg/L for Day 476.

5.3 Aquifer Layering and Solute Distribution

Patrick (1986) obtained a core from the Borden experimental site and measured hydraulic conductivity at 5 cm intervals by the method of Sudicky (1983). The core was retrieved from a location that was traversed by the 10% MTBE plumes of this study. As shown in Figure 5-11, the hydraulic conductivity profile obtained from the core has an upper section that, on average, has a hydraulic conductivity of about 12 m/day, and a lower section with an average hydraulic conductivity of about 6 m/day.

Vertical profiles of concentration data from a multilevel sampler (4A-N1) adjacent to the core location are also shown in Figure 5-11. Profiles for chloride, benzene, m-xylene, and dissolved oxygen are presented for the second and third sample events. The core is not ideally situated for this study, in that it was located near the margins of the plumes rather than in the center, but the relationship of solute distribution to aquifer layering can still be appreciated.

After 42 days, benzene and chloride are present in the upper, high hydraulic conductivity zone, while m-xylene, a more retarded solute, has not yet arrived. There are sharp contrasts in concentration with depth for all of the solutes, which suggests that they are traveling in discrete layers. Significant dissolved oxygen is available in the high hydraulic conductivity zone. Only minor amounts of benzene are detectable in the lower hydraulic conductivity zone.

By Day 106, chloride and benzene are nearly absent in the upper zone, having traveled beyond this location in the direction of flow. However, they remain in the lower zone at about half the concentrations observed on Day 42 in the upper zone. m-Xylene has arrived at the core location, but it persists only in the deeper, low hydraulic conductivity zone. Dissolved oxygen concentrations are now reduced in both the upper zone and the lower zone, perhaps because oxygen has been used for consumption of the monoaromatics.

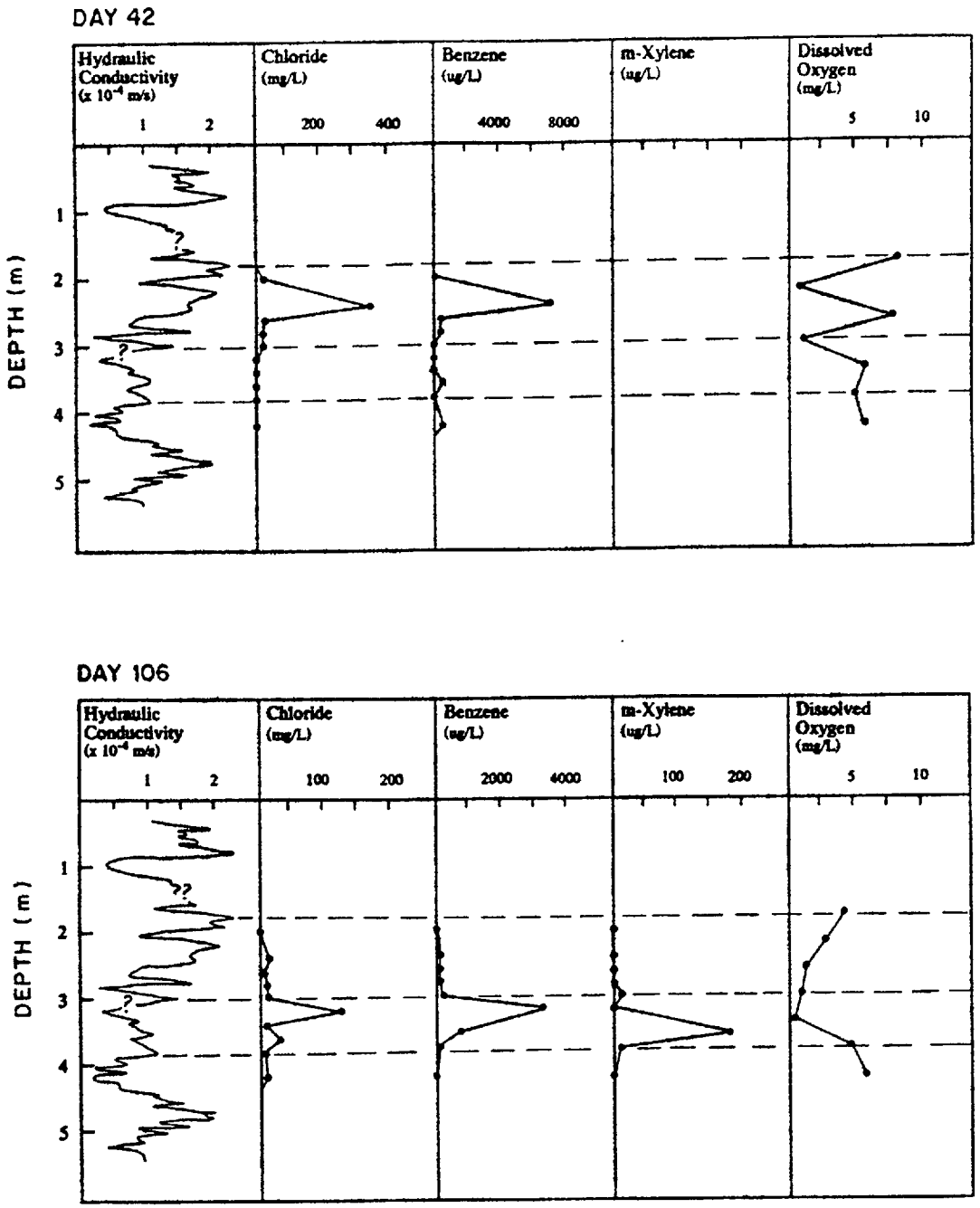


Figure 5-11. Profiles of hydraulic conductivity (after Patrick, 1986) and chloride, benzene, m-xylene, and dissolved oxygen concentration with depth at the sampler #4A-N1. Concentration data are shown for Days 42 and 106.

5.4 Summary and Discussion of Observations

Qualitative observations of the behavior of the three chloride tracers indicate that all of the plumes are migrating in a similar flow regime. The flow system, as manifested by the concentration distribution of the conservative tracer, includes a higher velocity zone overlying a lower velocity zone. The existence of these zones can be related to the hydraulic conductivity distribution of one core from the site, which has a section of high hydraulic conductivity (averaging 12 m/day) overlying a section of lower hydraulic conductivity (averaging about 6 m/day).

The velocity differential between the zones produces a bimodal concentration distribution of both chloride and the organic solutes in cross section, and enhances the longitudinal spreading of the plumes. An increase in the surface area of the plumes is also produced, providing greater potential for oxygen entry than would be available in a more homogeneous flow system.

Methanol and MTBE travel was not retarded in the aquifer, and neither has a discernible effect on the transport rates of BTEX. The monoaromatics separate with time, traveling at different rates according to their hydrophobicity, with benzene exhibiting the greatest mobility and the xylenes and ethylbenzene exhibiting the least.

No MTBE mass loss is distinguishable, while methanol mass loss occurs at a rapid rate. Methanol is only detectable in a few sample points by the final sample round. All of the monoaromatics lose mass over time. m-Xylene mass diminishes more rapidly than that of the other xylene isomers, and toluene is also rapidly degraded. Benzene appears relatively persistent, although some mass loss is evident. Benzene, and perhaps o-xylene, p-xylene, and ethylbenzene, are more persistent in the 85% methanol plume, indicating that the presence of methanol is inhibiting mass loss for these compounds.

For several of the organics, the rate of mass loss appears to be greater than the rate of spreading, particularly in the lateral and vertical directions. For the xylenes, compounds

that are highly retarded and also degrade rapidly, the plumes narrow dramatically. For benzene, particularly in the 85% methanol plume, degradation rates do not exceed the spreading rate, and spreading increases with time. For MTBE, which has no mass loss and travels unretarded, the plume length increases fivefold over sixteen months. Higher mobility and slower mass loss rates combine to increase the zone of impact of solutes such as benzene and MTBE.

Although the shapes of the organic plumes in large part mimic that of the chloride, indicating that heterogeneity of groundwater flow velocity is the major controlling factor in plume shape, some differences in vertical solute distribution among reactive and nonreactive solutes are evident. For example, concentration gradients are consistently steeper on the plume margins for the solutes undergoing mass loss than for the conservative tracer. This may be due to mass consumption on the plume margins where oxygen is most readily available. Furthermore, the organic solutes appear to be persisting in lens-shaped zones that are at the same scale as the structural bedding of the aquifer. As noted in Section 2, the concentration distribution of background dissolved oxygen exhibited a similar pattern. It is likely the spatial distributions of hydraulic conductivity, oxygen availability, and rate of biotransformation of the monoaromatics are interrelated.

Skewing of the mass distributions is evident through time for the reactive solutes, but not for the conservative tracer. The benzene and toluene plumes have tailing at the back through time, while the xylenes and ethylbenzene plumes exhibit a tailing of the distribution toward the front. The cause of the skew in mass distributions for the monoaromatics is not immediately apparent: it may result from a combination of transport phenomena and uneven loss of mass. For methanol, the forward tailing of mass distribution can be attributed to uneven loss of mass, since this compound travels unretarded in the aquifer and the conservative tracer exhibits no skew. In subsequent sections, these qualitative observations of solute behavior are examined more rigorously using quantitative estimates of transport and fate parameters obtained from the spatial moment analysis.

Section 6
TRANSPORT OF THE SOLUTES

There are three processes that directly affect solute transport in the Borden aquifer: advection, dispersion, and sorption. Advection is the transport of solutes by groundwater flow and, for purposes of this study, is estimated as the velocity of the center of mass of a solute pulse. Dispersion is the spreading of solutes about the center of mass. It results from mechanical mixing due to groundwater velocity variations at the pore, lens, and layer scale, and from diffusion due to chemical concentration gradients. Sorption is the partitioning of reactive solutes between the groundwater and the aquifer medium. It causes a reduction in the average solute migration rate which can be quantified through comparison of relative velocities of the reactive solutes and the conservative tracer.

This section describes the transport of the solutes using quantitative estimates of average horizontal solute velocities, retardation factors, and dispersion parameters obtained by spatial moment estimation. Transport of the chloride tracers is examined to establish whether the solutes in the three test cases migrated at similar rates and encountered the same degree of aquifer heterogeneity. The transport of the reactive solutes is described primarily to identify any differences in BTEX transport that result from the presence of the oxygenates. Secondary objectives of this section are to compare field estimates of retardation to laboratory predictions, to identify whether retardation of the solutes shows time-dependence, and to determine whether there is any relationship between transport behavior and observed mass losses for the reactive solutes.

6.1 Horizontal Center of Mass Trajectories

The horizontal trajectories of the centers of mass of the chloride plumes are shown in Figure 6-1. The travel paths were parallel, and curved slightly to the east, with the easterly shift in direction occurring sometime between the third and fourth sampling rounds (between Day 106 and 317). For all three plumes, the angle of the mean velocity vector was approximately 11° east of the y axis of the monitoring network.

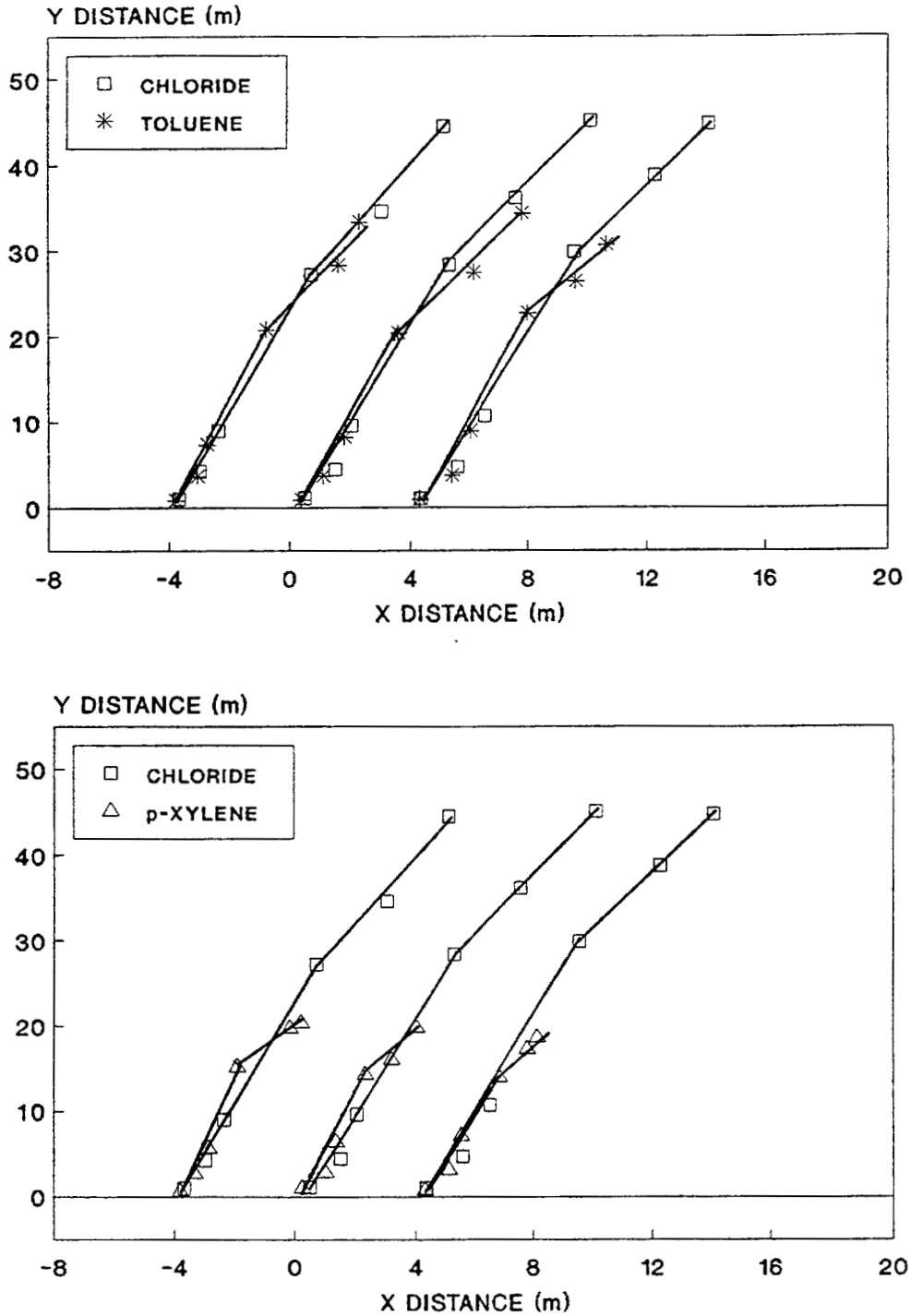


Figure 6-1. Center of mass trajectories for the chloride, toluene, and p-xylene plumes.

Figure 6-1 also shows the toluene and p-xylene center of mass trajectories. At early times, the paths of the organic solutes were collinear with the chloride trajectories. At late times, the centers of mass of the reactive solutes were offset from the chloride trajectory, typically in an easterly direction. During previous tests at the site, deviations from collinearity of reactive and nonreactive solute trajectories were not observed (Mackay *et al.*, 1986; Patrick, 1986).

The differences in solute trajectory observed in this experiment are consistent with a directional change in hydraulic gradient. Mackay *et al.* (1986) monitored water levels at the site and found that the direction of the hydraulic gradient varied seasonally by as much as 14°. During this experiment the reactive solutes lagged further and further behind the nonreactive tracer with time. They would therefore have occupied a different position in the aquifer during a change in gradient than the chloride, and the bend in their travel path would occur at a location closer to the injection zone. Furthermore, the reactive solutes would be retarded with respect to the lateral component of transport, so the bend in travel path would be less sharp than that of the chloride. Under this scenario, collinearity of the organics trajectory with the chloride trajectory would not be expected following a directional shift in hydraulic gradient if it occurred after the plumes had become separated in space.

Preferential degradation of one side of a reactive plume could also result in a center of mass trajectory that is offset from that of the chloride tracer. For example, if more oxygen were available on one side of a plume, a sideways skew in mass distribution could result. This scenario could explain individual instances of center of mass positions that are not aligned with the chloride trajectory, but cannot account for the systematic differences observed.

6.2 Velocities of Plume Movement

The distances traveled by the center of mass of each solute plume are tabulated in Appendix G. Center of mass positions are reported as distance from the central injection

well. Figures 6-2 and 6-3 show plots of distance traveled over time for six solutes in each of the test cases.

Chloride Tracers. The three chloride plumes traveled about 40 meters over the sixteen month experiment. Since chloride is nonreactive in this system, the chloride velocities should reflect average pore water velocities over the vertical extent of the chloride plumes. As shown in Figures 6-2 and 6-3, the distance vs. time plots for chloride are essentially linear, indicating a relatively constant horizontal groundwater velocity field over the zone traversed by the chloride plumes. The chloride plumes were about ten times thicker than the vertical hydraulic conductivity correlation length, so it can be assumed that they encompassed a significant proportion of the groundwater velocity distribution.

Velocities of bulk solute movement can be calculated by dividing distance traveled by time for a given sampling event. Calculation of solute velocity in this manner assumes a steady, homogeneous pore water velocity field and transport governed by classic advection and dispersion. Chloride center of mass velocities for each experimental time interval are listed in Table 6-1. Note that the velocities between Day 1 and Day 6 appear anomalously high: it is likely that these values do not reflect the natural gradient, but are an artifact of injection hydraulics.

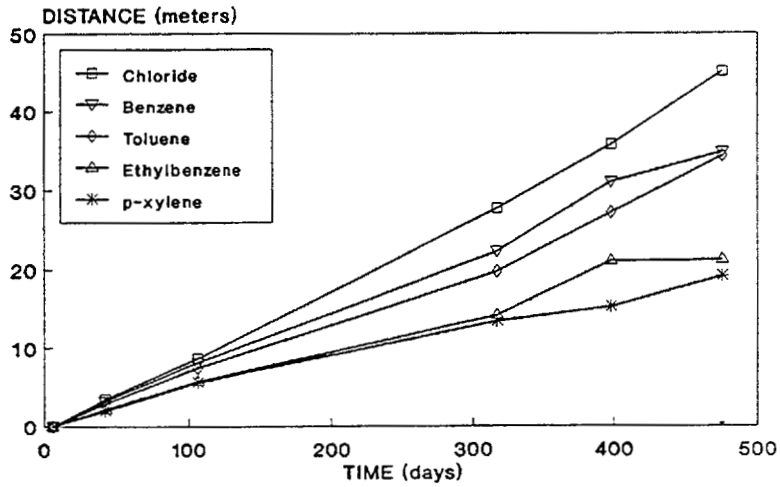
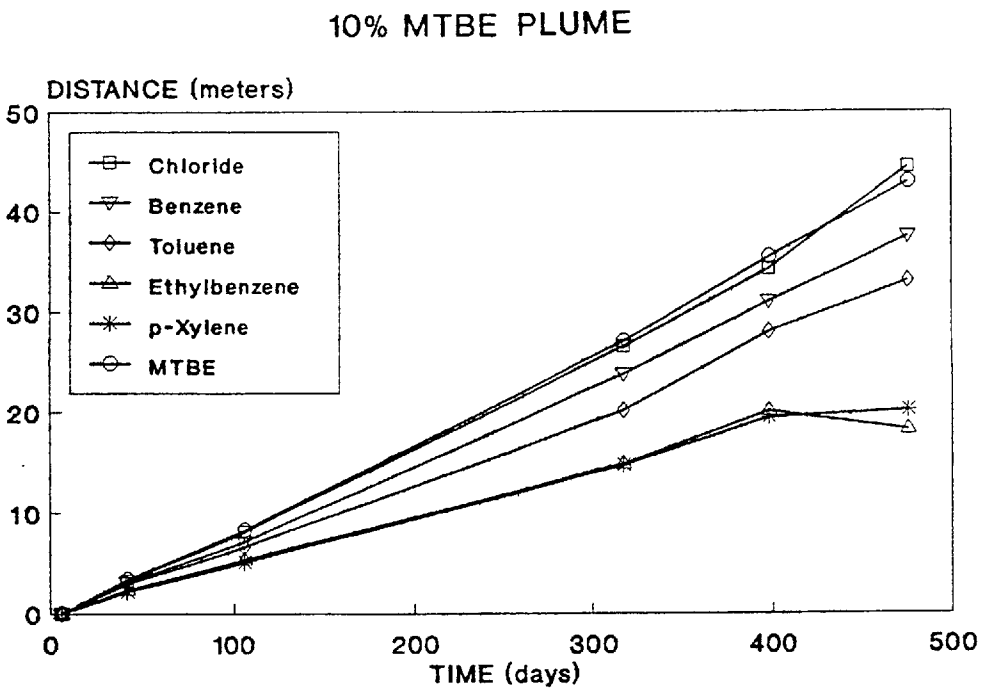


Figure 6-2. Plot of distance traveled vs. time for solutes in the 100% PS-6 gasoline control plume.



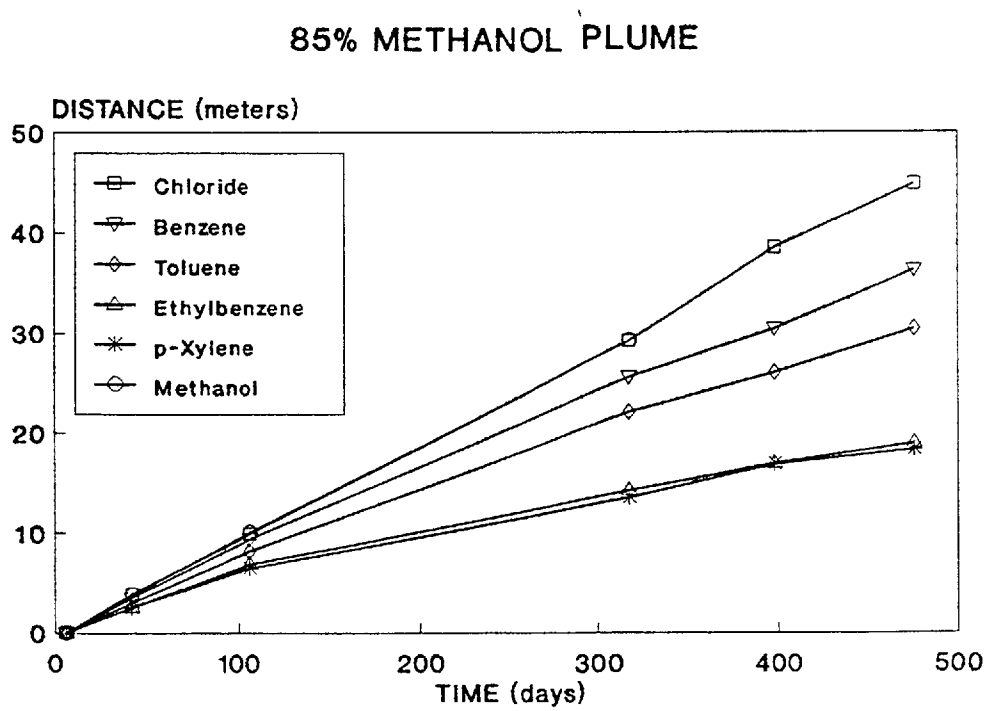


Figure 6-3. Plots of distance traveled vs. time for solutes in the 10% MTBE and 85% methanol plumes.

Table 6-1. Horizontal Velocities of the Chloride Plumes (cm/day).

Interval of Days Since Injection	90% PS-6 plus 10% MTBE Plume	100% PS-6 Plume	15% PS-6 85% Methanol Plume
0 to 6	17.23	20.07	18.08
6 to 42	9.14	9.58	10.81
42 to 106	7.52	8.05	9.36
106 to 317	8.75	9.06	9.17
317 to 398	9.48	9.97	11.52
398 to 476	13.02	11.92	8.05
6 to 476	9.33	9.47	9.42

Patrick (1986) noted a slight velocity decline for the chloride tracer over 100 days of travel in a natural gradient tracer test conducted in 1985 in the vicinity of the 10% MTBE and 100% PS-6 injections of this study, and he reported an average linear groundwater velocity of 0.08 m/day. A minor velocity decline was also noted for that portion of the aquifer in this study over an equivalent time period (Table 6-1). However, velocities subsequently increased, yielding an average of about 0.09 m/day for each of the chloride plumes over the sixteen month experiment. This average is the same as that observed in a previous two-year test at the site (Mackay *et al.* 1986).

At the start of the experiment, there was some concern that the width of the three plumes would be too narrow relative to the lateral hydraulic conductivity correlation length (2.8 m), and they would therefore encounter differing velocity zones. For example, in a natural gradient experiment with a chloride tracer in a nearby test area, Sudicky (1983) noted adjacent "fast" and "slow" zones that were not detectable by standard hydrogeological measurement techniques. Average velocities of the chloride plumes in this study were remarkably similar, indicating that the experimental design criterion of comparability of flow regime for the three cases was met.

Oxygenates. MTBE traveled at the same velocity as the chloride tracer over the course of the experiment. As shown in Figure 6-3, the distance traveled versus time plot of MTBE essentially matches that of chloride. Methanol also traveled with chloride, but by the final two sampling events there was little detectable methanol and the center of mass positions were not quantified.

Monoaromatics. The monoaromatics traveled at varying velocities. Benzene was transported the greatest distance in the flow system, about 35 meters. The xylenes and ethylbenzene traveled the smallest distance, about 20 meters. As shown in Figures 6-2 and 6-3, there is a small reduction in transport velocity for these solutes with time relative to the chloride tracer. Roberts *et al.* (1986) also noted a reduction in solute velocity with time for organic solutes in this test area along with a constant chloride velocity.

There were no detectable differences in velocities of the monoaromatics in the 10% MTBE or 85% methanol cases relative to the control case. Such differences were not discernible even at early times when the monoaromatics occupied the same portion of the aquifer as the oxygenates, and the concentrations of the oxygenates were at their highest level.

6.3 Field Retardation

The relative mobilities of the organic solutes can be quantified by determining retardation factors (R). These can be estimated as ratios of the plume transport velocities:

$$\mathbf{R} = \frac{\text{velocity of chloride center of mass}}{\text{velocity of organic solute center of mass}}$$

The retardation factor for chloride is assumed to be unity, since it does not react with the aquifer solids. Table 6-2 summarizes the range of average retardation factors calculated for each compound in each plume. Retardation factors calculated for individual time periods are tabulated in Appendix G. For plumes with little mass remaining at late times, retardation was not quantified.

The retardation estimates for BTEX in the control plume (PS-6 gasoline) compare favorably to those observed in previous experiments at the site (Patrick *et al.*, 1986; Berry-Spark *et al.*, 1987). Benzene travels at about 91% of the rate of the chloride tracer, toluene at about 83%, and ethylbenzene and the xylenes at about 67% of the chloride tracer rate.

Table 6-2. Range of Average Field Retardation Factors Calculated for the Organic Solutes.

Solute	15% MTBE	100% PS-6	85% Methanol
MTBE	0.97 - 1.04	----------	----------
Methanol	----------	----------	0.99 - 1.04
Benzene	1.05 - 1.19	1.06 - 1.29	1.05 - 1.27
Toluene	1.13 - 1.34	1.16 - 1.40	1.21 - 1.48
Ethylbenzene	1.37 - 2.43	1.52 - 2.13	1.45 - 2.37
p-Xylene	1.52 - 2.20	1.56 - 2.35	1.53 - 2.45
m-Xylene	1.34 - 1.47	1.53 - 1.87	1.52 - 2.10
o-Xylene	1.38 - 1.97	1.51 - 2.19	1.45 - 2.13

The retardation factors of the two oxygenates did not deviate significantly from unity (Table 6-2), so they had no measurable interaction with the aquifer solids. Any enhancement of BTEX mobility due to oxygenate presence was expected to occur within the first three sampling events, when the oxygenate concentrations remained high and all of the solutes occupied the same volume of the aquifer. Table 6-3 shows average retardation factors through Day 106 for BTEX in the three test cases. No effects of the oxygenates on BTEX migration are discernible.

Table 6-3. Average Retardation Factors for the Organic Solutes from Day 6 to 106.

Solute	90% PS-6 10% MTBE	100% PS-6	15% PS-6 85% Methanol
MTBE	1.0	---	---
Methanol	---	---	1.0
Benzene	1.1	1.1	1.1
Toluene	1.2	1.2	1.2
Ethyl-benzene	1.5	1.5	1.4
p-Xylene	1.6	1.5	1.5
m-Xylene	1.5	1.5	1.5
o-Xylene	1.5	1.5	1.4

6.4 Laboratory Sorption Experiments

In laboratory sorption experiments, distribution coefficients (K_ds) for the monoaromatics were determined using the batch equilibrium method, in which the amount of sorption is inferred from changes in solute concentrations. BTEX solutions containing methanol and MTBE at concentrations that matched levels of the field injection were tested, along with a control case with no oxygenates. Borden aquifer material was used as the sorbent.

BTEX distribution coefficients obtained experimentally were higher for the case with no oxygenates than for the cases in which MTBE and methanol are present, indicating that the oxygenates have potential to decrease the affinity of BTEX for the solid phase. Theoretical calculations showed that, at the concentrations of methanol and MTBE in the field solutions, the distribution coefficients could be reduced by about 3-5%, and the experimentally determined K_ds are consistent with this finding. However, there was significant scatter in the data, and the differences among the test cases were not observed in a second experiment using a soil with a greater organic carbon content.

In order to compare the laboratory measurements of sorption to the mobility of the solutes in the field, laboratory K_ds were converted to estimates of field retardation factor using the following equation:

$$R = 1 + \frac{\rho K_d}{\theta}$$

where ρ is the bulk density of the soil and Θ is the porosity.

Use of K_ds to predict field retardation requires the assumption that partitioning of the solutes to the solid phase is instantaneous and reversible, and follows a linear isotherm. In fact the lab data for this study showed a slight decrease in sorption with increasing concentration, but previous experiments with BTEX and Borden sand have indicated that sorption of the monoaromatics can be adequately described by a linear isotherm (Gillham *et al.*, 1987). Values of bulk density and porosity for the Borden aquifer are 1.81 g/cm^3 and 0.33, respectively (Table 2-1). Estimates of retardation factor based on the laboratory results are presented in Table 6-4.

Predictions of retardation factors from the laboratory data fall within the range of calculated field retardation factors, but in general, the laboratory predictions are at the high end of the range observed in the field. For the more mobile solutes, benzene and toluene, the laboratory results lead to a consistent overprediction of field retardation.

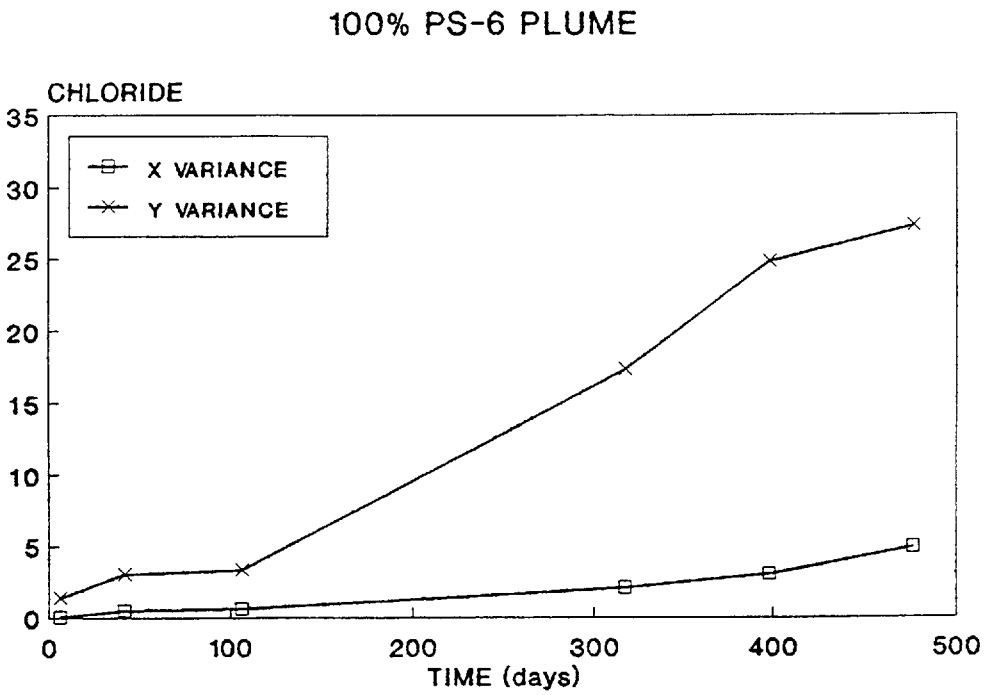
Table 6-4. Retardation Factors Calculated from K_ds.

SOLUTE	90% PS-6 10% MTBE	100% PS-6	15% PS-6 85% Methanol
Benzene	1.2	1.5	1.2
Toluene	1.3	1.5	1.4
Ethyl-benzene	1.7	1.8	1.5
p-Xylene	1.9	2.0	1.5
m-Xylene	1.8	2.0	1.7
o-Xylene	1.5	1.7	1.6

6.5 Spatial Variance and Dispersion

The spatial moment analysis yielded estimates of spatial variance for each of the solute plumes. Since the focus of the analysis was on obtaining accurate estimates of solute mass, the estimates of spatial variance should be treated with caution. In future work with the data, these estimates can be refined. Although the data are preliminary, plots of spatial variance over time can be used to illustrate the general trends in spreading behavior of the solutes. The x variance provides a measure of the lateral spreading of the solutes about the center of mass, while the y variance reflects longitudinal spreading.

Figure 6-4 shows the x and y variance for chloride in the 85% methanol and control plumes. The variances are reported in the field coordinate system. Longitudinal dispersion is clearly greater than lateral dispersion, and the two plumes have comparable degrees of spreading. The evolution of the spatial variance estimates is consistent with observations of the changes in shape of the chloride distributions with time. The curves are concave upward, indicating a slight increase in the spreading rate with time.



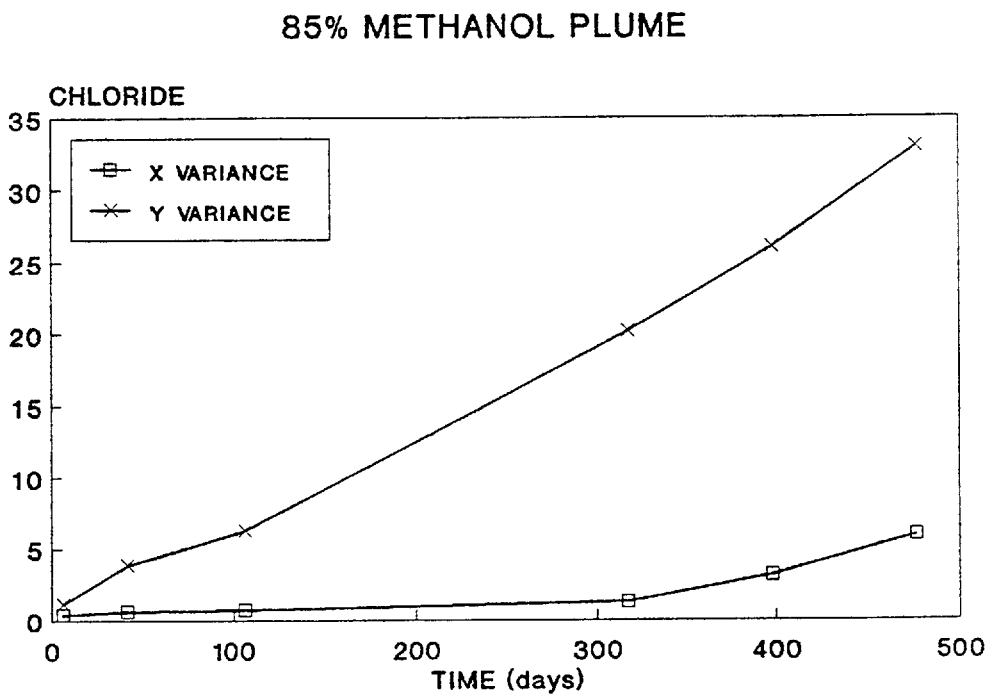


Figure 6-4. Longitudinal and horizontal transverse variance for chloride in the 100% PS-6 gasoline control and the 85% methanol cases.

Apparent longitudinal and transverse dispersivities can be calculated by dividing the average linear groundwater velocity by half the slope of the best-fit line passing through the points. This calculation method neglects molecular diffusion. It also assumes that the average linear velocity is constant in time, a reasonable assumption based on the near linearity of distance traveled vs. time plots for the chloride tracers (Fig. 6-2, 6-3). As discussed in Freyberg (1986), the following equation is used to calculate dispersivities from the plots of spatial variance:

$$A = \frac{1}{2} \frac{d}{dt}\left(\frac{\sigma}{v}\right)$$

where A = apparent dispersivity
σ = spatial variance
v = average linear groundwater velocity

Values calculated for principal components of the dispersivity tensor for the three test cases are shown in Table 6-5. The components of the dispersivity tensor were estimated using the field coordinate system and then rotated 11° clockwise to realign the coordinate system with the estimated mean groundwater velocity vector, using a standard cartesian tensor rotation.

The calculated dispersivities are consistent with those obtained by Freyberg (1986) over a similar travel distance at the same site, although the values of transverse dispersivity are smaller. This may be an artifact of the calculation method. The similarity in dispersivities for the three cases of this study indicates the plumes are encountering the same degree of aquifer heterogeneity along their travel paths.

Table 6-5. Dispersivities of Freyberg (1986) and This Study

Case	Longitudinal Dispersivity (m)	Horizontal Transverse Dispersivity (m)
Freyberg (1986)	0.36	0.037
15% MTBE 100% PS-6 85% Methanol	0.30 0.35 0.39	0.030 0.028 0.031

In the case of the reactive solutes, the x and y variances are not necessarily a direct reflection of dispersion. Mass loss complicates the analysis of dispersion and so the organic solutes are not considered here.

6.6 Summary and Discussion of Solute Transport Findings

Average linear groundwater velocities, calculated using the velocity of the center of mass of the conservative tracers over the sixteen month test, were about 9 cm per day for all three plumes. The degree of spreading of the chloride plumes, as manifested in the change in longitudinal and transverse spatial variance with time, was similar for the three cases. The calculated longitudinal and transverse dispersivities were similar for the three test cases and compared favorably to previous dispersivity estimates for the Borden aquifer. These findings confirm that the three plumes traveled in a similar flow system and encountered the same degree of aquifer heterogeneity.

Methanol and MTBE traveled unretarded in the aquifer, while the monoaromatics were retarded to varying degrees depending on their hydrophobicity. Benzene was the most mobile with a retardation factor of 1.1, and ethylbenzene and the three xylene isomers were the least mobile, with retardation factors of about 1.5. Retardation factors for the monoaromatics averaged over the first 106 days of transport were similar to those observed in previous studies.

The oxygenates did not cause a measurable difference in retardation of the monoaromatics relative to the control case, even at early times when all of the solutes occupied the same volume of the aquifer and oxygenate concentrations were at their highest. Laboratory sorption experiments showed a small potential for both oxygenates (at injected concentrations) to decrease the distribution coefficients of BTEX, but this effect was not measurable in the field.

API (1991) showed that cosolubility effects of methanol become important only at aqueous methanol concentrations above 25%, and influences on BTEX mobility can also

be expected at this level. It is therefore likely that increases in mobility of the monoaromatics would only be observed close to a subsurface source of an 85% methanol/15% gasoline mixture.

Retardation factors for discrete time intervals were variable. They generally increased with time for all of the monoaromatics in all three cases, and the effect was most pronounced for the highly retarded solutes. The apparent time dependence of retardation cannot be linked to a specific process. Diffusive uptake into the internal porosity of the sand grains is a relatively unlikely mechanism since BTEX retardation factors calculated from field data were smaller than those calculated from lab data. In order to attribute time-dependent changes in retardation to time-dependent changes in soil-water partitioning, it must be assumed that the organic and the conservative tracer are moving in identical groundwater velocity fields at any given time, since R is calculated as a ratio of solute velocities. However, in this experiment, biotransformation of the monoaromatics may have influenced their transport rate relative to that of chloride.

For example, the observed changes in retardation could have been related to the reducing vertical thickness of the biodegrading plumes: as mass was consumed, the plumes narrowed in the vertical direction, and they were subject to a more local velocity field than the chloride plumes, which essentially maintained their thicknesses, or expanded due to vertical transverse dispersion. The relative reduction in velocity observed for the xylenes may have occurred because the plumes were consumed preferentially from high velocity zones and persisted in lower velocity zones. High velocity zones are more rapidly replenished by nutrients and oxygen, and may support more active microbial populations.

Section 7
ESTIMATES OF SOLUTE MASS

This section presents observations of the changes in mass with time for each of the solutes. Rates of mass loss are calculated, and differences among the three test cases are noted. In general, the spatial moment analysis yielded estimates of solute mass that are consistent with the descriptive understanding of the plumes available from contour plots of the mass distributions. Processes contributing to the observed rates of mass loss are discussed in subsequent sections.

7.1 Estimates of Injected Mass

The concentrations of the solutes fluctuated during the injection. In order to obtain the best possible estimate of injected mass, plots of concentration vs. elapsed injection time were made for each compound. Elapsed time was defined as the period during which water was actually entering the injection wells: pauses due to equipment difficulties were subtracted. The area under the curves was then calculated with a program written by R. Devlin and multiplied by the flow rates to obtain mass estimates. The program uses a cubic spline routine to obtain the area under the curve. Table 7-1 shows estimates of the total mass injected for each solute.

Table 7-1. Estimates of Injected Mass (grams).

Solute	90% PS-6 10% MTBE	100% PS-6	15% PS-6 85% Methanol
Chloride	1,200	980	1,500
MTBE Methanol	670 ---	--- ---	--- 18,300
Benzene Toluene Ethylbenzene p-Xylene m-Xylene o-Xylene	21.8 15.2 2.7 2.7 7.0 3.9	20.4 14.0 2.3 2.3 5.8 3.4	21.9 14.6 2.3 2.3 5.9 3.3
Total BTEX	53.3	48.2	50.3
Dissolved Oxygen	6.4	7.2	8.7

7.2 Mass Estimates for the Sample Rounds

Estimates of the mass of each compound in solution at each sampling event, obtained from the spatial moment analysis, are tabulated in Appendix G. For the nonsorbing solutes, chloride and the oxygenates, the masses of the compounds in solution represent their total mass in the system. For the sorbing solutes, a portion of the mass will sorb to the aquifer material following solute injection.

The ratio between the total mass sorbed and the mass in solution is equal to the retardation factor for solute transport in the aquifer. For example, the xylenes have a retardation factor of 1.5, so at any one time, 50% of the mass of a xylene plume will be sorbed to the aquifer material. The total mass of a solute present at a given time can be approximated by:

Total Mass = (Retardation Factor) * (Mass in Solution)

Roberts *et al.* (1986), in a comparable natural gradient tracer test at the Borden site, used retardation factors computed for each time to determine the total mass at each time. As discussed in Section 6, the variable retardation factors observed for the final three sample rounds of this study are not necessarily attributable to variability in soil-water partitioning. The average retardation factors from the first three sample rounds, (prior to significant loss of solute mass), are more reliable indicators of sorptive partitioning, so these were used to calculate total plume masses. Use of this method of mass approximation assumes that soil-water partitioning is instantaneous and reversible, and that the partitioning coefficient does not change with time.

Chloride Tracers. Table 7-2 lists the estimates of chloride mass for each of the time intervals, and Figures 7-1 and 7-2 show plots of chloride mass vs. time for each of the three chloride plumes. For the fourth sample round, the sample points in the monitoring network were not sufficiently deep to fully penetrate the chloride plumes for the 10% MTBE and 100% PS-6 gasoline cases, so the mass estimates appear low. In sample round

five, all three chloride plumes were incompletely captured. By sample round six, all three chloride plumes intersected a deeper portion of the monitoring network, and they were entirely captured. The mass estimates for the five instances of incomplete plume capture are shown in Figures 7-1 and 7-2 with an arrow pointing upward to indicate that they represent minimum values.

Table 7-2. Estimates of Total Chloride Mass for Each Sample Time (kg)

Test Case	Days Since Injection						Avg.
	6	42	106	317	398	476	
10% MTBE	1.41	1.13	1.15	0.78*	0.65*	1.39	1.27
100% PS-6	1.08	1.27	0.97	0.63*	0.51*	1.50	1.09
85% MEOH	1.35	1.44	1.50	1.65	0.85*	1.32	1.32

* The plumes extended below the base of the monitoring network for these sampling events. These values were not included in the calculation of average mass.

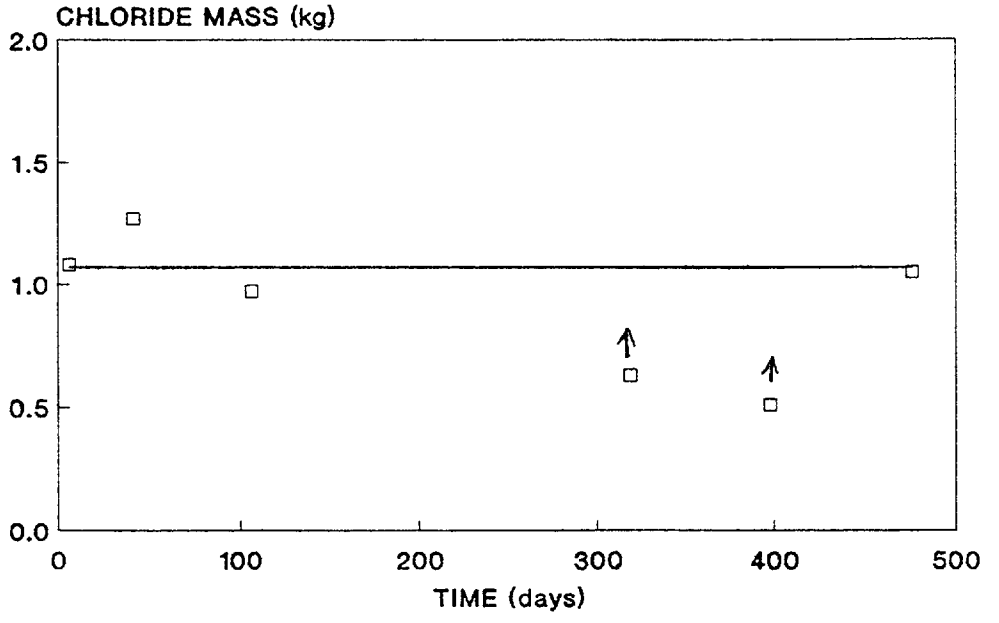


Figure 7-1. Plots of mass vs. time for chloride in the 100% PS-6 gasoline control plume. Upward arrows indicate the chloride plume was incompletely captured and mass estimate represents a minimum value. The line is the average mass for the sample rounds in which the plumes were entirely captured.

The estimated total mass was expected to be constant with time for chloride since it is nonreactive in this aquifer. If the cases of incomplete capture are discounted, the average of the remaining values can be compared to the injected mass for an indication of the reliability of the mass estimation procedure. As shown in Table 7-2, the average chloride masses were estimated at 1.27 kg for the 10% MTBE case, 1.09 kg for the 100% PS-6 control case, and 1.45 kg for the 85% methanol case. These masses compare favorably with the estimated injected masses (Table 7-1). They are 6% and 10% greater than the injected mass for the 10% MTBE and 100% PS-6 cases, and 3% lower for the 85% methanol case. Thus the estimation of the mass of the compounds in solution by Freyberg's technique has given results that are consistent with the expected behavior of the conservative tracer.

Methanol and MTBE. Plots of mass vs. time for the oxygenates are presented in Figure 7-3, and the mass values are given in Table 7-3. The MTBE plume traveled with the chloride plume throughout the experiment, residing in the same locations in the monitoring network at each sample event. It can therefore be assumed that the problem of incomplete capture of the chloride plume encountered in the fourth and fifth sample rounds also applies to the MTBE plume, and that the proportions of mass captured should be the same. In order to provide a realistic estimate of the persistence of MTBE through time, the MTBE mass at these two times was normalized to the chloride mass using the following equation:

$$M_n(t) = \frac{Cl(0)}{Cl(t)} * M(t)$$

where $M_n(t)$ is the normalized organic mass at time t; M(t) is the apparent organic mass at time t; Cl(0) is the initial chloride mass; and Cl(t) is the apparent chloride mass at time t.

The mass estimate for the methanol plume in the fifth sample round was not subject to the normalization procedure, even though the methanol also traveled with the chloride and chloride was incompletely captured on that date. This is because so little methanol mass remained at that time that proportionality of capture could not be assumed.

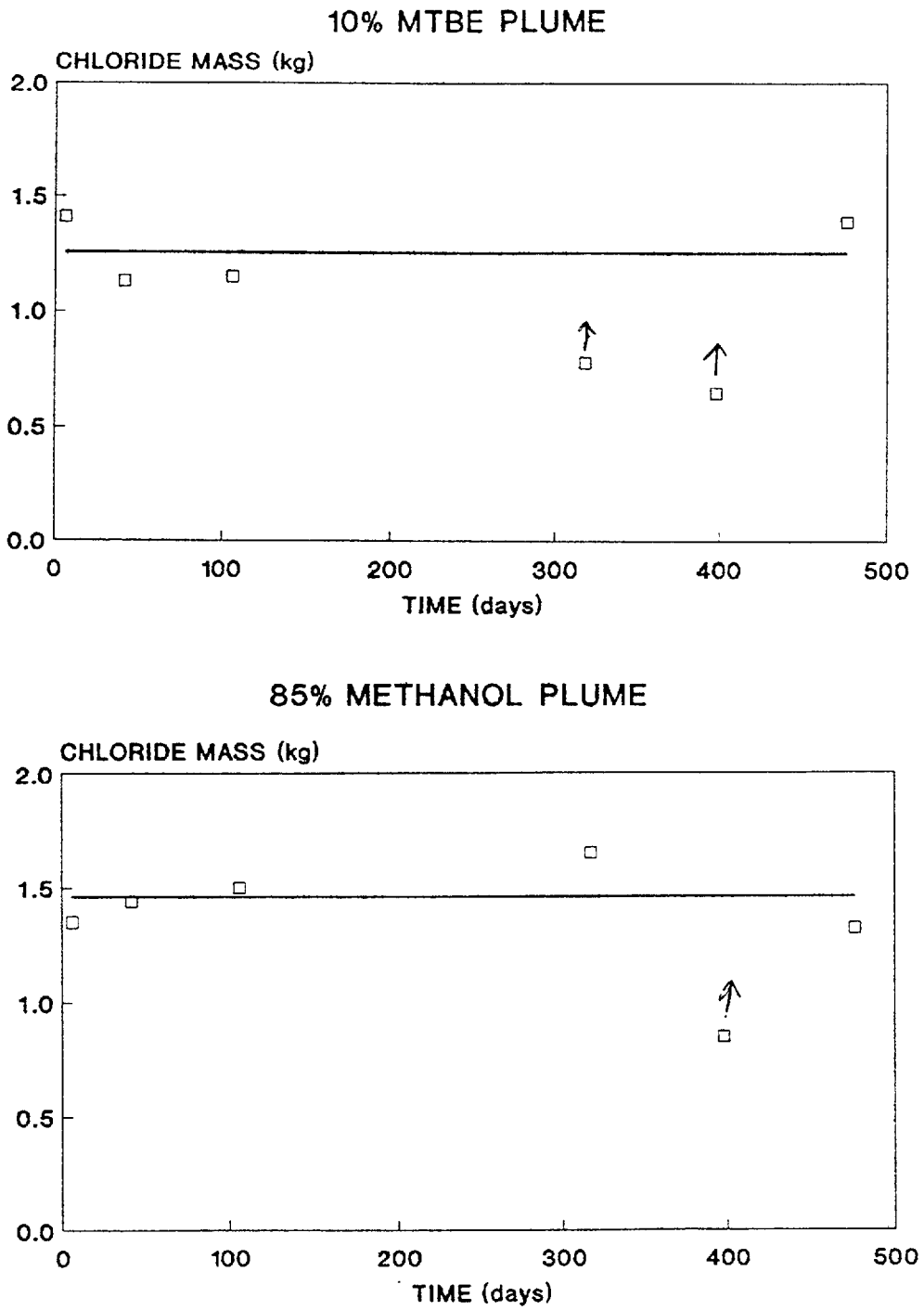


Figure 7-2. Plots of mass vs. time for chloride in the 10% MTBE and 85% methanol plumes. Upward arrows indicate the chloride plume was incompletely captured and mass estimate represents a minimum value. The line is the average mass for the sample rounds in which the plumes were entirely captured.

Table 7-3. Estimates of Total Oxygenate Mass for Each Sample Time (kg)

Oxygenate	Days Since Injection						Avg.
	6	42	106	317	398	476	
MTBE	0.70	0.70	0.67	0.36*	0.34*	0.60	0.67
Methanol	13.56	14.44	13.44	3.59	0.09	0.01	NA

* The plumes extended below the base of the monitoring network for these sample events. These values were not included in calculation of the average MTBE mass.
NA = not applicable

Over the sixteen month experiment, MTBE showed no evidence of mass loss. The calculated mean mass of the MTBE over time is 0.67 kg, which equals the estimated injected mass. The methanol mass remained constant at about 13-14 kilograms through Day 106, and then diminished rapidly. The estimated methanol mass for the first three sample rounds is lower than the injected mass (18.3 kg) by several kilograms, and it is unlikely that such a large amount of methanol could have been transformed within just six days: it is more likely that the estimate of injected mass is inaccurate. The constant mass estimated through Day 106 represents a lag period preceding the onset of detectable mass loss. There was such a long break in sampling after the third sample round that the precise duration of the lag period cannot be determined, but it was at least 106 days. Following the initial lag, methanol was rapidly transformed. Only 25% of its mass remained by Day 317, and less than 1% remained by the final sample round.

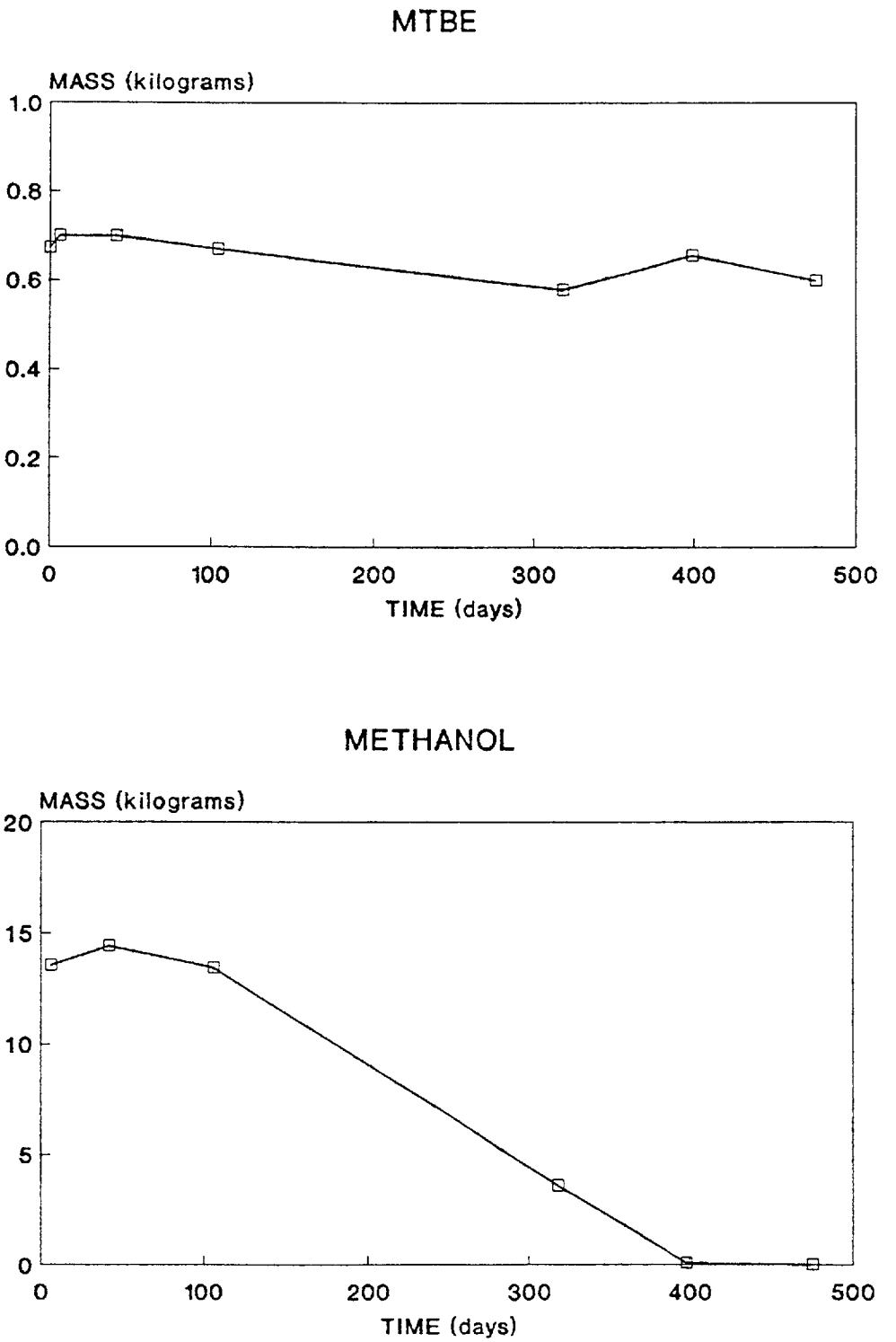


Figure 7-3. Plots of mass vs. time for MTBE and methanol. MTBE data for days 317 and 398 are adjusted. See text for details.

Monoaromatics. Table 7-4 lists the total masses estimated for BTEX, and Figures 7-4 to 7-9 depict mass losses of the monoaromatics through time. The mass loss curves for the monoaromatics in the two cases containing the oxygenates are presented with the control case for comparison.

As shown in Figure 7-4, benzene was removed at approximately the same rate in the control (100% PS-6) plume and the 10% MTBE plume, following an apparent lag period of about 40 days. After sixteen months, less than 20% of the initial mass remained in the 100% PS-6 and 10% MTBE cases. Benzene mass diminished more slowly in the 85% methanol case: by the final sample event, more than 50% of the mass remained. In all three cases, the mass loss was essentially linear. The ethylbenzene, p-xylene, and o-xylene mass loss curves were similar to that for benzene in that they were linear, and the rate of mass loss was slower for the 85% methanol case (Figures 7-5 through 7-7).

Toluene mass loss curves were nearly identical for all three cases (Figure 7-8), and the shape of the curves was concave upward rather than linear. Toluene loss was initially very rapid, followed by tailing at late times. Only 50% of the toluene mass remained by Day 106, and by the final sample round more than 95% of the toluene had been removed. The mass loss curves for m-xylene were similar to those for toluene in that the initial loss was rapid, followed by tailing (Figure 7-9). Substantial differences among the three m-xylene curves were not evident, and no measurable m-xylene mass remained by the final sample round.

Table 7-4. Estimates of Total Mass for BTEX at each Sample Time (grams).

10% MTBE CASE

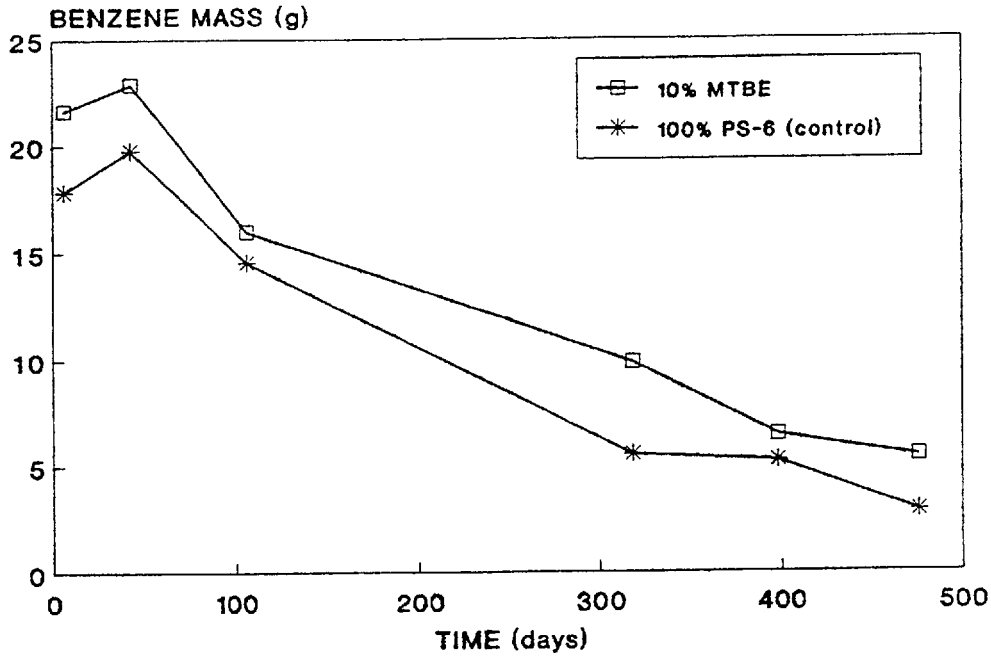
Solute	Day 6	Day 42	Day 106	Day 317	Day 398	Day 476
Benzene	21.6	22.9	15.9	9.9	6.4	5.5
Toluene	13.9	17.1	8.1	1.4	0.8	0.2
Ethylbenzene	2.5	2.5	1.8	0.7	0.3	0.08
p-Xylene	2.5	2.9	1.9	0.8	0.3	0.2
m-Xylene	6.7	6.7	2.9	0.3	0.2	0.0
o-Xylene	3.6	4.2	2.9	1.0	0.6	0.3

100% PS-6 GASOLINE CASE

Solute	Day 6	Day 42	Day 106	Day 317	Day 398	Day 476
Benzene	17.8	19.8	14.5	5.5	5.2	2.9
Toluene	12.7	11.2	9.4	1.4	0.1	0.02
Ethylbenzene	2.6	2.2	1.8	0.9	0.1	0.06
p-Xylene	2.5	2.2	1.9	0.8	0.1	0.1
m-Xylene	6.5	6.0	3.4	0.4	0.1	0.0
o-Xylene	3.8	3.6	2.9	1.4	0.3	0.3

85% METHANOL CASE

Solute	Day 6	Day 42	Day 106	Day 317	Day 398	Day 476
Benzene	16.1	19.1	17.5	12.0	9.8	10.2
Toluene	11.0	13.9	10.2	2.2	0.6	0.2
Ethylbenzene	2.0	2.2	1.4	1.0	0.7	0.6
p-Xylene	1.9	2.4	1.4	0.8	0.7	0.5
m-Xylene	5.0	6.1	3.3	0.6	0.1	0.0
o-Xylene	2.8	3.6	2.4	1.4	1.1	0.5



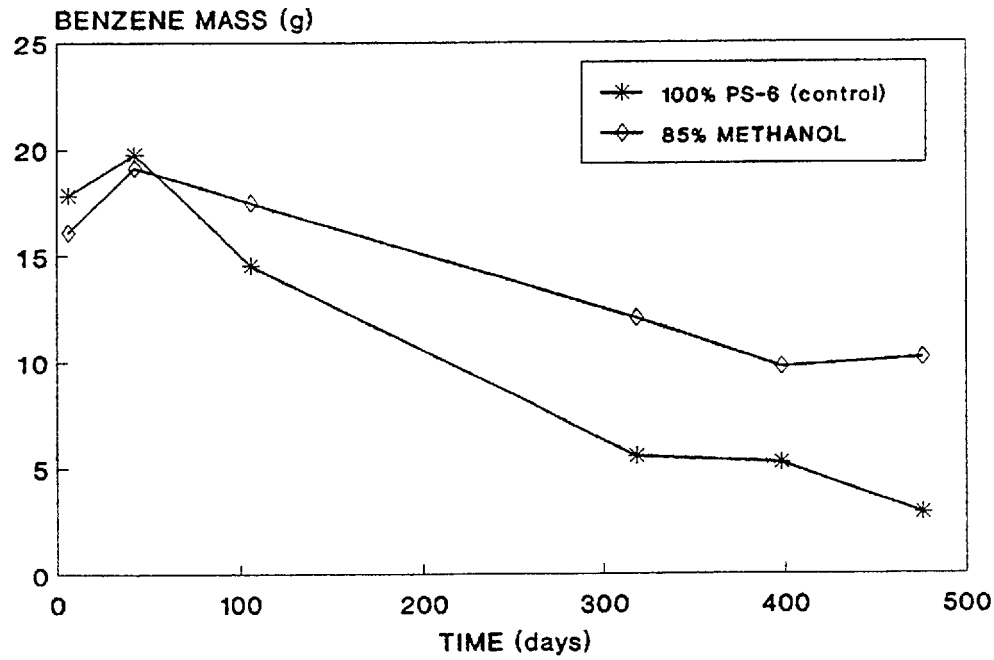


Figure 7-4. Plots of benzene mass vs. time for the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control.

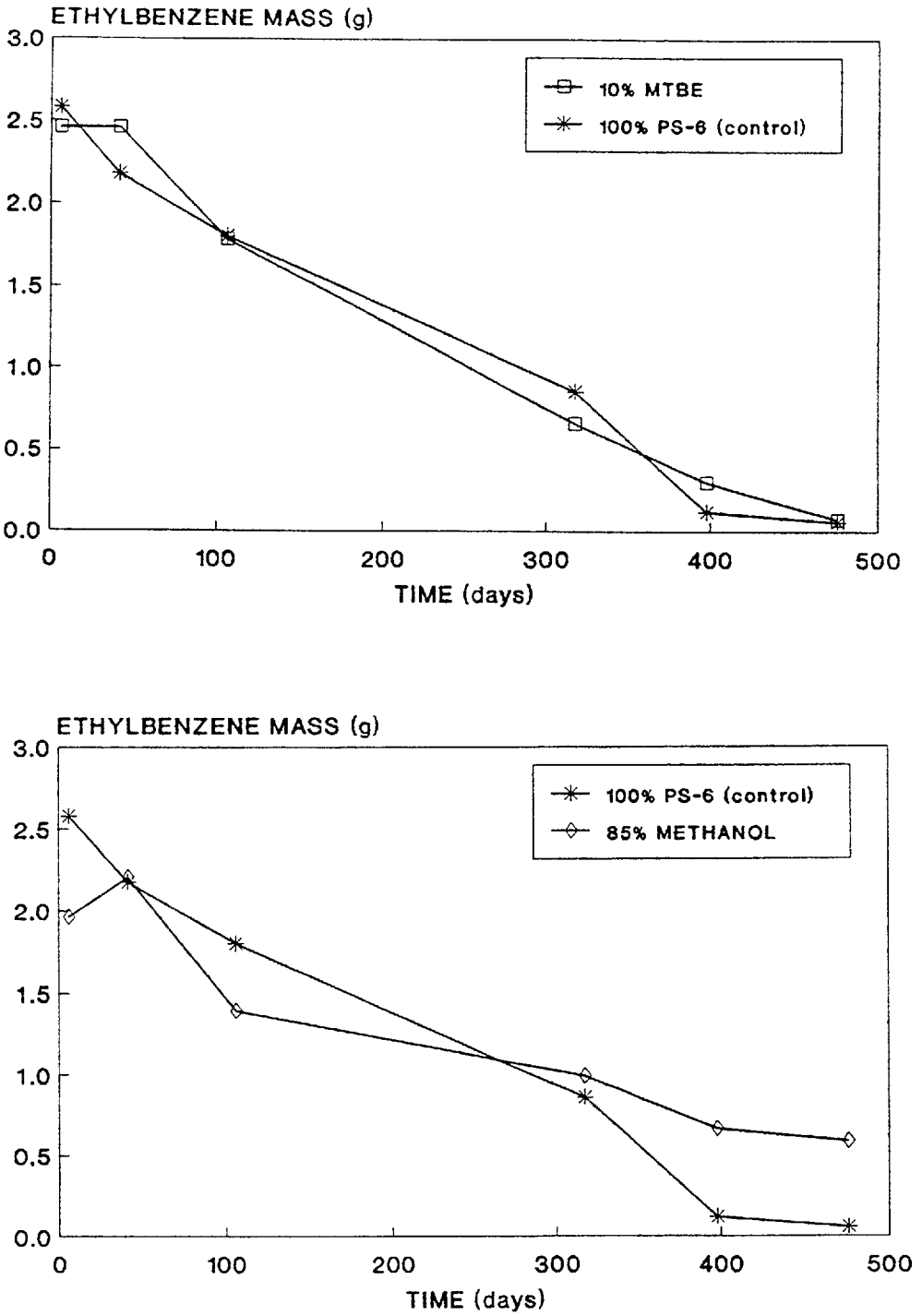
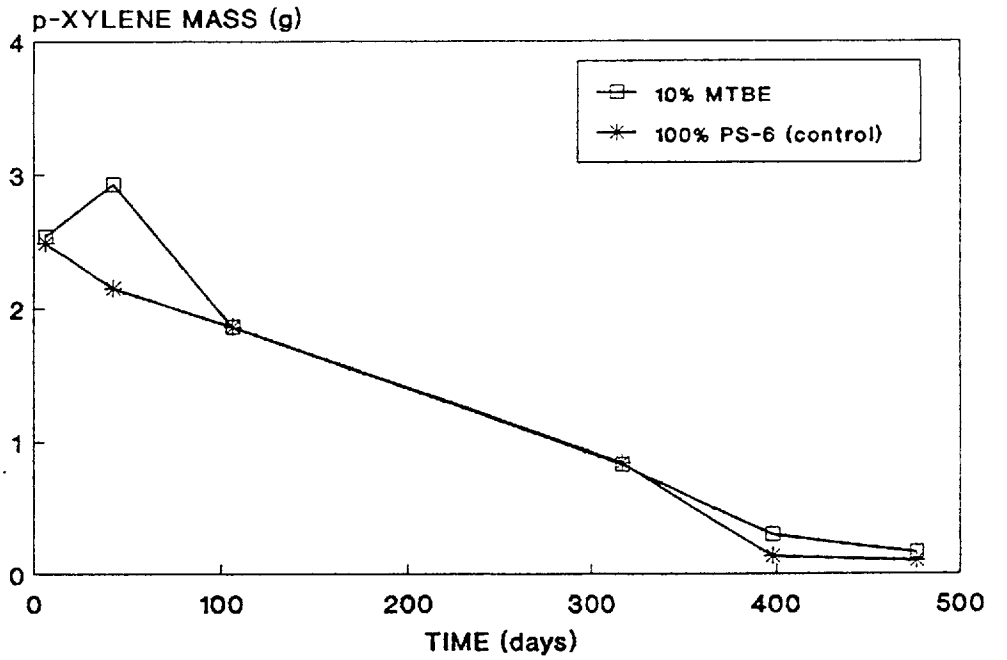


Figure 7-5. Plots of ethylbenzene mass vs. time for the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control.



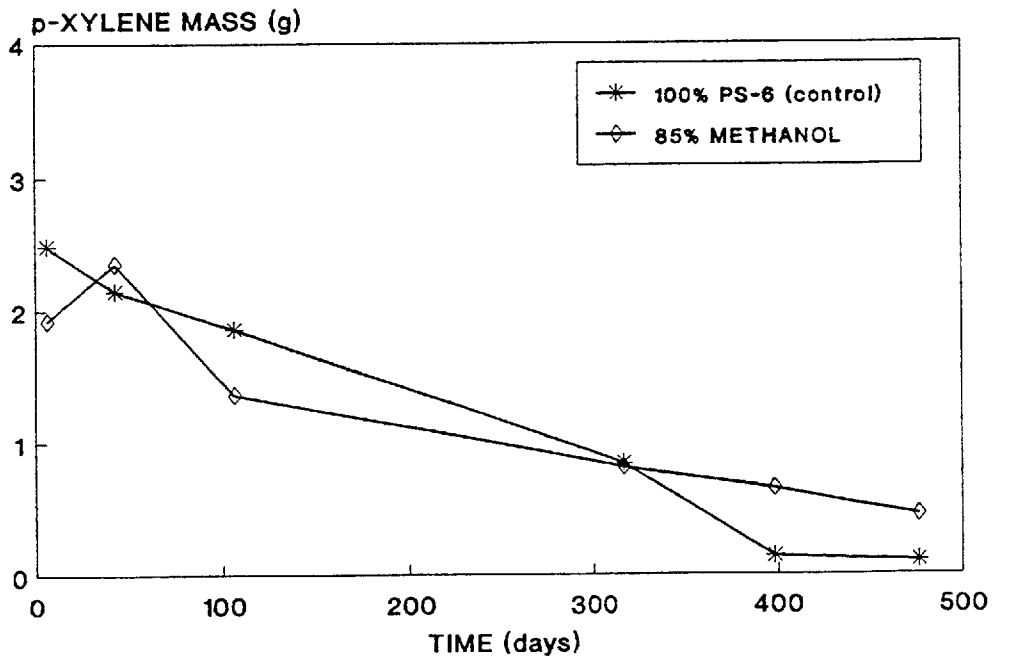
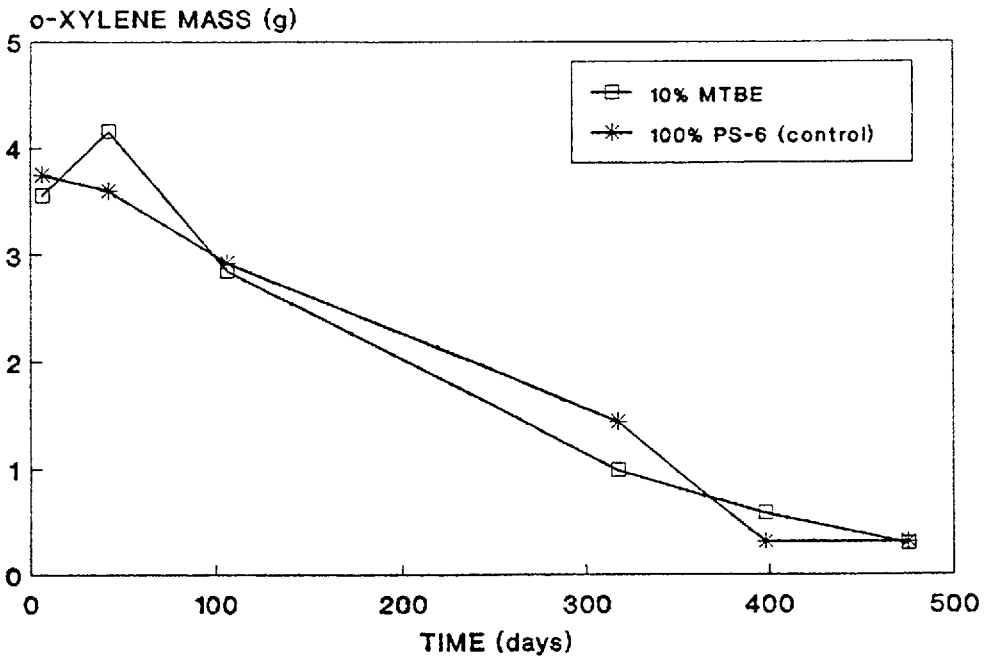


Figure 7-6. Plots of p-xylene mass vs. time for the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control.



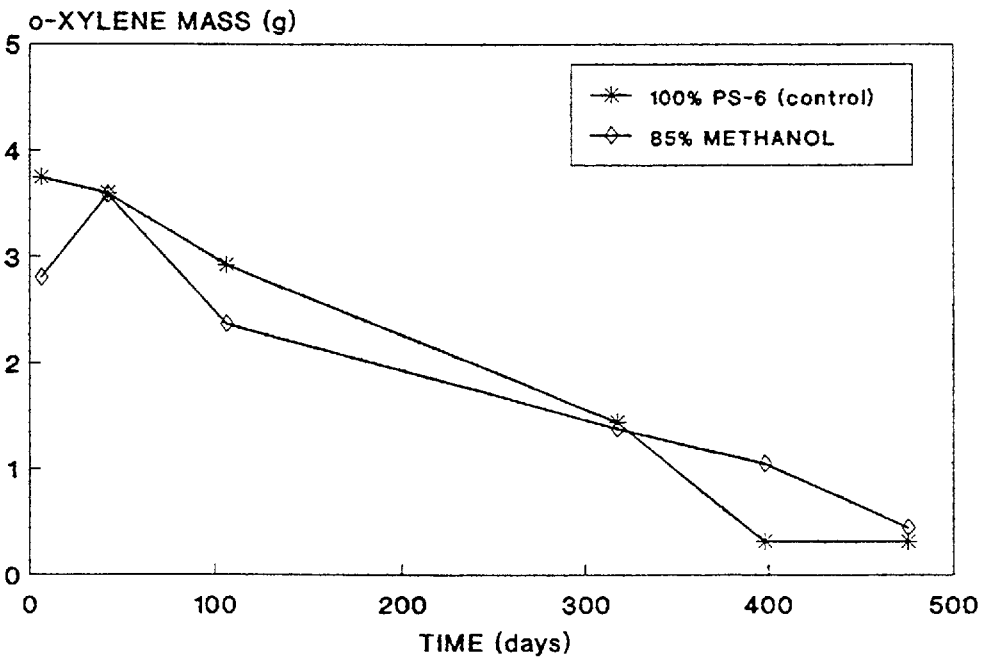
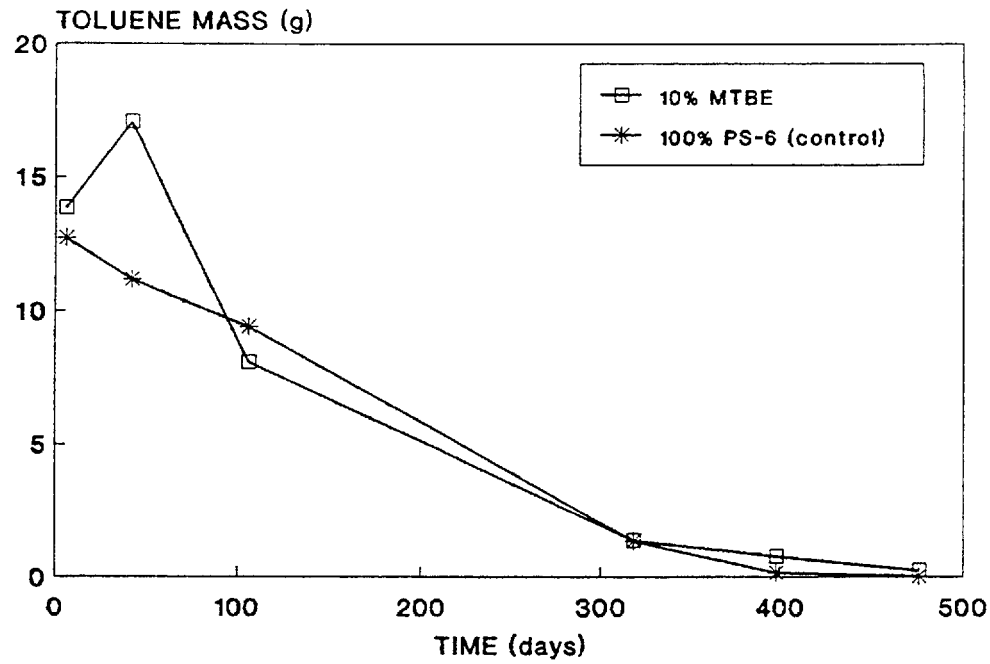


Figure 7-7. Plots of o-xylene mass vs. time in the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control.



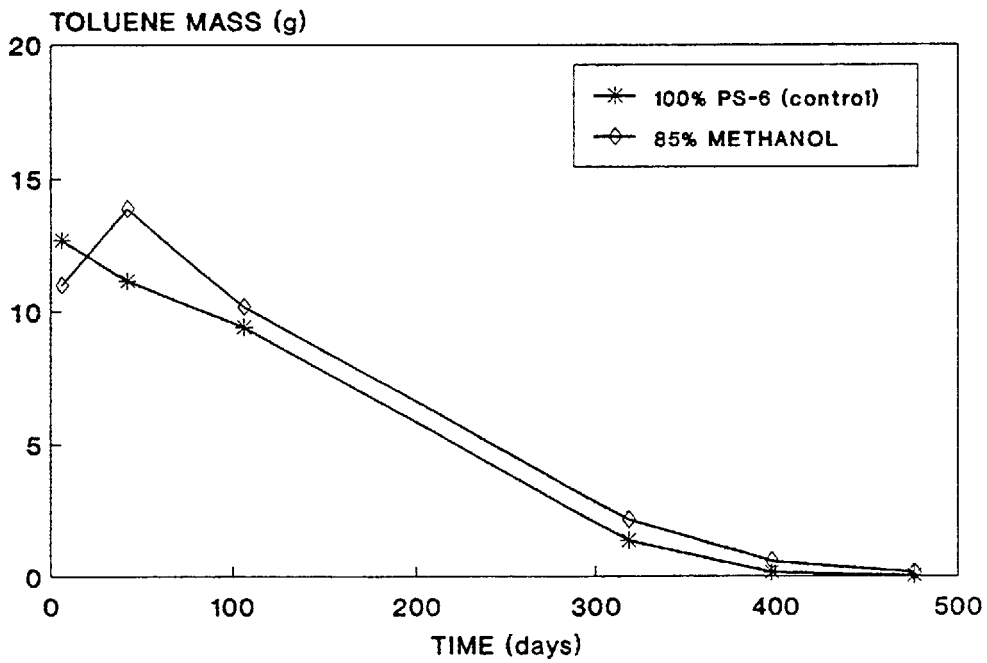
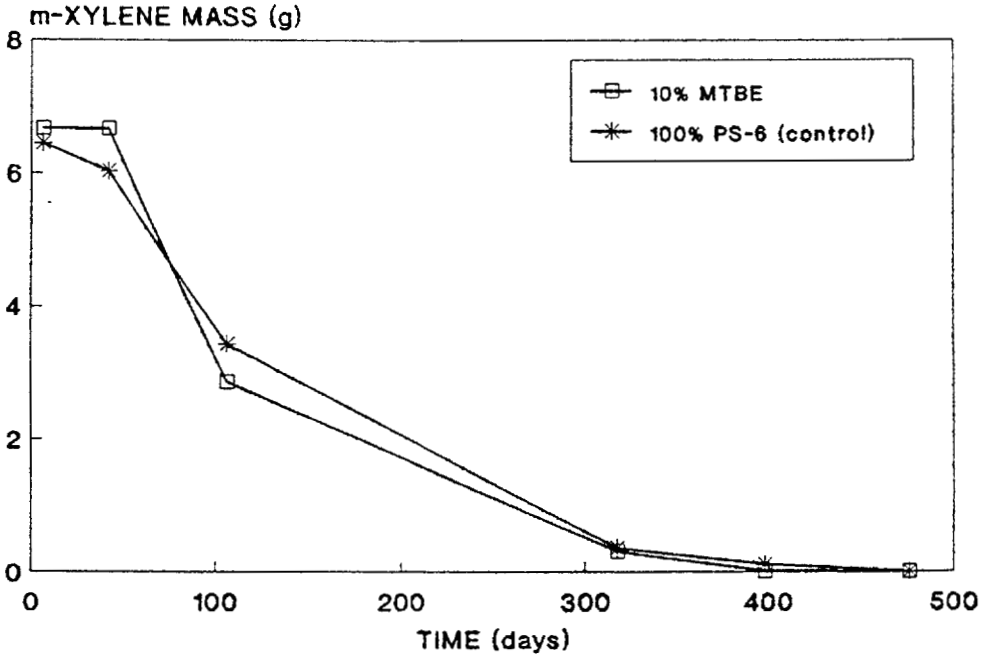


Figure 7-8. Plots of toluene mass vs. time in the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control.



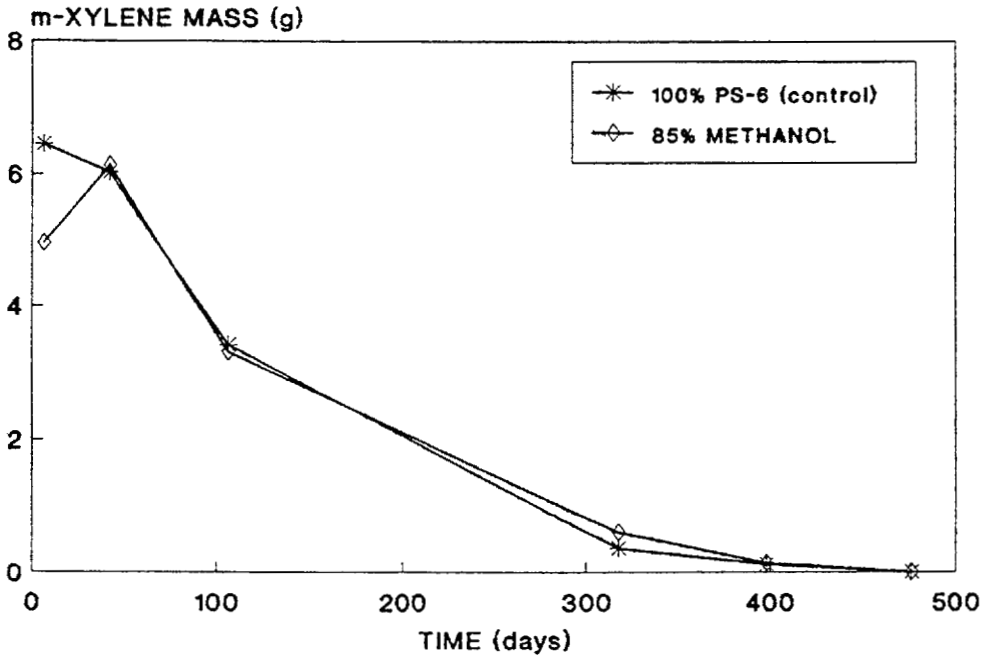


Figure 7-9. Plots of m-xylene mass vs. time in the 10% MTBE and 85% methanol plumes as compared to the 100% PS-6 control.

7.3 Rates of Mass Loss

In order to compare the rates of mass loss of BTEX in each of the test cases, the mass loss curves were described with both zero order and first order equations. Zero order rate constants were obtained by performing linear regressions on the plots of total mass vs. time and determining the slopes. For toluene and m-xylene, lines were fit only to the early, steep portion of the curves. First order rate constants were obtained by performing a linear regression on the log mass vs. time data and determining the slopes. Only the post-lag data were used in rate estimation.

Coefficient of determination (r^2) values were excellent, for both the linear and log-linear regressions, ranging from 0.89 to 0.98, but they were consistently better for the log linear case. In addition, lines could be fit to the full range of the toluene and m-xylene data using log mass. For purposes of comparing the various cases, only the first order rates will be presented (Table 7-5). Use of these models to describe the curves does not imply that first order or zero order biotransformation processes are responsible for the observed mass losses. Many factors are expected to contribute to the shape of the solute mass loss curves from pulse input sources. MacQuarrie and Sudicky (1990), in modelling the transport and aerobic biotransformation of a single organic solute in the Borden aquifer, found that the rate of mass loss at the plume scale is relatively insensitive to kinetic parameters of biotransformation. More important factors governing the rate of mass loss and the shape of the mass loss curves included average groundwater flow velocity and dispersion parameters, oxygen availability, substrate concentration, and hydrophobicity of the compound.

In order to compare the absolute rates of mass loss, a t-test was performed to determine whether there was a significant difference in the slopes of the lines fit to the log mass vs. time data. BTEX mass loss rates for the control case were tested against those for the 10% MTBE and 85% methanol cases to quantify the effects of oxygenate presence on persistence of the monoaromatics.

Table 7-5. First Order Mass Loss Rates (day^{-1}) Calculated for Day 6 through Day 476.

SOLUTE	90% PS-6 10% MTBE	100% PS-6	15% PS-6 85% Methanol
MTBE	NA	---	---
Methanol	---	---	0.019
Benzene	0.003	0.004	0.001**
Toluene	0.009	0.013	0.009
Ethylbenzene	0.007	0.008	0.003*
p-Xylene	0.006	0.007	0.003*
m-Xylene	0.014	0.010	0.009
o-Xylene	0.005	0.006	0.004

* Significantly different from the control at a 1% probability level.
** Significantly different from the control at a 0.1% probability level.

The mass losses of the monoaromatics in the 100% PS-6 gasoline control case occurred at differing rates. Toluene and m-xylene mass loss was the most rapid: both solutes were nearly undetectable by the final sample round. Benzene, the monoaromatic of greatest concern to human health, was the most recalcitrant.

There were no measurable changes in MTBE mass over the six month experiment, and it is possible that loss of MTBE mass occurred at a rate that was too slow to detect in this study.

Mass loss rates of the monoaromatics in the 10% MTBE case did not differ significantly from those of the control case (Table 7-5). Thus, under the conditions of this experiment, MTBE does not measurably influence mass loss rates for BTEX.

After the initial 100-day period in which the methanol mass remained constant, methanol was transformed at a rapid rate, (0.019 day^{-1}). At the close of the 16-month experiment, less than 1% of the methanol mass remained. Methanol presence had no measurable impact on the rates of mass loss of toluene and m- and o-xylene. A t-test showed that

benzene mass loss rates were significantly reduced relative to the control. P-xylene and ethylbenzene mass loss rates were reduced to a lesser extent, although the reduction was still statistically significant.

7.4 Discussion of Mass Loss Findings

The relative rates of biotransformation for the monoaromatics in all three test cases, from most rapid to slowest were as follows:

$$\text{Toluene} \\ \text{m-Xylene} \end{matrix} > \begin{matrix} \text{Ethylbenzene} \\ \text{p-Xylene} \\ \text{o-Xylene} \end{matrix} > \text{Benzene}$$

These relative biotransformation rates did not correlate to hydrophobicity of the compounds or to initial substrate concentrations, but the pattern was consistent in all three test cases. The oxygenates, therefore, had no influence on the relative rates of biotransformation of the monoaromatics.

Oxygenate persistence was very different for the two compounds under study: MTBE was entirely recalcitrant, while methanol was transformed at a rapid rate following an initial three and a half month lag period. Effects of the oxygenates on the absolute rates of BTEX biotransformation were also different for the 85% methanol and 10% MTBE cases. MTBE presence had no measurable effect, while the rate of benzene mass loss was reduced significantly in the 85% methanol plume. Removal of p-xylene and ethyl-benzene mass was also slowed in the presence of methanol. The mechanisms responsible for the increased persistence of benzene in the 85% methanol plume may be related to inhibitory effects of the methanol on microbial populations or to oxygen depletion in the 85% methanol plume.

In order to attribute differences in mass loss rates to geochemical factors such as changes in oxygen concentration or methanol presence, transport parameters must be considered equivalent for the plumes containing oxygenates and that of the control: hydrogeological

parameters must be ruled out as experimental variables. Calculated values of average linear groundwater velocity and dispersivity were found to be essentially equal for the three test cases, implying that the three plumes encountered the same degree of aquifer heterogeneity along their travel paths (Section 6). The observed differences in mass losses are therefore attributable to geochemical factors.

To further explore the geochemical influences on the removal of solute mass in the field, a series of laboratory biotransformation experiments were performed. These experiments, described in Supplemental Appendix H of this report, and reviewed in Section 8, were intended to provide confirmation that biotransformation is the mechanism responsible for the observed mass losses, and to explore some of the potential geochemical controls on solute biotransformation.

Section 8
LABORATORY BIOTRANSFORMATION STUDY

A laboratory study was undertaken to assess the ability of the subsurface microbial population at the Borden site to degrade the contaminants of concern in the field experiment. The study also investigated two potential constraints on metabolism of the monoaromatic hydrocarbons:

- the availability of oxygen as an electron acceptor; and
- the potential for methanol or MTBE to act as preferred substrates or microbial growth inhibitors.

Details of the experimental design, methods, data interpretation techniques, and results are presented in supplemental Appendix H to this study, available under separate cover. This section presents summary information on the laboratory study and illustrates the key findings with conceptual diagrams.

8.1 Experimental Approach and Design

Microcosms -- sealed bottles containing aquifer soil and water -- were used in the laboratory biotransformation experiments. Through the use of sterile controls, microcosms permit isolation of biotransformation from other mass loss processes.

The microcosms of this study were designed to represent the shallow, aerobic portion of the Borden aquifer where the field experiment was conducted. Soil and groundwater were taken from the same depth interval as the field injection zone, and the microcosms remained static throughout the study to simulate subsurface conditions. Microcosms were incubated in the dark at 10°C, the average temperature of the Borden aquifer.

In order to ensure comparability with the field experiment, initial concentrations of the organics in the microcosms were similar to those in the field injection solutions. As in the field experiment, fuel-contacted groundwater was diluted to obtain the desired concentrations. One fuel that was not part of the field study, a blend of 15% methanol

and 85% PS-6 gasoline, was included in the laboratory study in order to evaluate the effects of methanol at a lower aqueous concentration than that produced by the 85% methanol blend.

Previous work at the Borden site has shown that the transport of oxygen into dissolved gasoline plumes is the rate-controlling factor in BTEX biodegradation when no oxygenates are present (Patrick, 1986; MacQuarrie *et al.*, 1990). Static microcosms are therefore unlikely to produce accurate estimates of field mass loss rates. Static microcosms do, however, provide a means for evaluating the physical and chemical constraints on BTEX biodegradation, and can help define the expected limits to in situ bioremediation of the monoaromatics in the presence of oxygenates.

Two chemical constraints on BTEX biodegradation were explored in this study: the presence of oxygenates as potential microbial growth inhibitors or preferred substrates, and the need for oxygen as the key electron acceptor. Persistence of the monoaromatics in microcosms containing methanol or MTBE was compared to BTEX persistence in baseline microcosms containing no oxygenates. One set of microcosms was incubated with an unlimited supply of oxygen, while a second had a limited oxygen supply.

The unlimited oxygen experiment was intended to represent conditions at the edge of a gasoline plume, where oxygen is available by diffusion from uncontaminated groundwater or admixture due to dispersion. It tested whether methanol or MTBE influences BTEX biotransformation when oxygen availability is not a constraint, and whether the oxygenates themselves biodegrade under conditions in which oxygen is plentiful.

The limited oxygen experiment simulated conditions at the center of a gasoline plume, where oxygen is likely to become depleted as the compounds are biotransformed. This experiment permitted observation of the changing patterns of BTEX and oxygenate biodegradation as oxygen became unavailable for aerobic biotransformation. In particular, it tested whether the microbial population in the aerobic zone of the Borden aquifer is

capable of using alternative electron acceptors to transform either the oxygenates or the monoaromatics.

8.2 Interpretation of Microcosm Data

The microcosm approach constitutes a batch determination of the ability of a microbial population to degrade a compound within a given timeframe and under a specific set of environmental conditions. Two parameters are established from microcosm studies: the acclimation period prior to any observable biodegradation of a compound, and the subsequent rate of biotransformation. Together these factors describe the persistence of the compound in the microcosm.

There are several mechanisms which may account for the acclimation period commonly observed before the onset of detectable biodegradation. It may represent the time needed for enzyme induction or genetic alterations. Time may be required before a degrader population becomes sufficiently large to produce a measurable biodegradation rate. Environmental factors, such as insufficient nutrients or preferential substrate utilization, may also play a role. Time may also be needed for the degraders to acclimate to inhibitors in their environment (Wiggins *et al.*, 1987).

Many of the factors that have potential to cause or prolong an acclimation period can also affect rates of biotransformation. In this study, persistence of the organic solutes is influenced by the presence of the oxygenates (potential microbial growth inhibitors or preferred substrates) and the availability of a key electron acceptor (oxygen). Changes in solute persistence which are of a magnitude that will affect subsurface travel distances are of greatest interest. Groundwater at the CFB Borden field site flows at about 9 cm/day, so factors which increase (or decrease) persistence on the order of months (rather than days or weeks) can be considered significant.

8.3 Biotransformation of the Monoaromatics

The persistence of the monoaromatics in microcosms containing no oxygenates varied depending on the availability of oxygen. Figure 8-1 provides an conceptual illustration of the biotransformation of benzene, toluene, and m-xylene under conditions of unlimited oxygen and limited oxygen. The diagrams are based on data provided in Appendix B. For the limited oxygen case, the duration of the aerobic period is shown for reference.

With unlimited oxygen (Figure 8-1a), BTEX biodegraded rapidly, and no acclimation period was observed for any of the compounds. Most of the mass loss occurred within two months. In general, the rate of first order aerobic biotransformation was similar for all six compounds, ranging from 0.024 day^{-1} to 0.038 day^{-1}. Minor differences in biotransformation rates for the compounds included a more rapid rate of loss for toluene and m-xylene, and a slower rate of loss for benzene.

More rapid biotransformation of m-xylene relative to the other xylenes has also been reported by Kappeler and Wuhrman (1978). The meta isomer is apparently more susceptible to microbial attack in some environments. The small variations in relative rate of biotransformation for the compounds of this study had little effect on their overall persistence in the microcosms when oxygen availability was unlimited.

Under oxygen-limited conditions, dissolved oxygen was depleted in the microcosms within one week, and biotransformation of the monoaromatics was observed during the aerobic period only (Figure 8-1b). No BTEX mass losses were detected during the subsequent 15-month anaerobic period.

A mass balance of BTEX loss and oxygen consumed showed that at least some of the oxygen in the microcosms was used for metabolism of other solutes. Demands for oxygen could come from other dissolved constituents of the gasoline or from the naturally occurring organic content of the water or the soil. Low molecular weight, readily

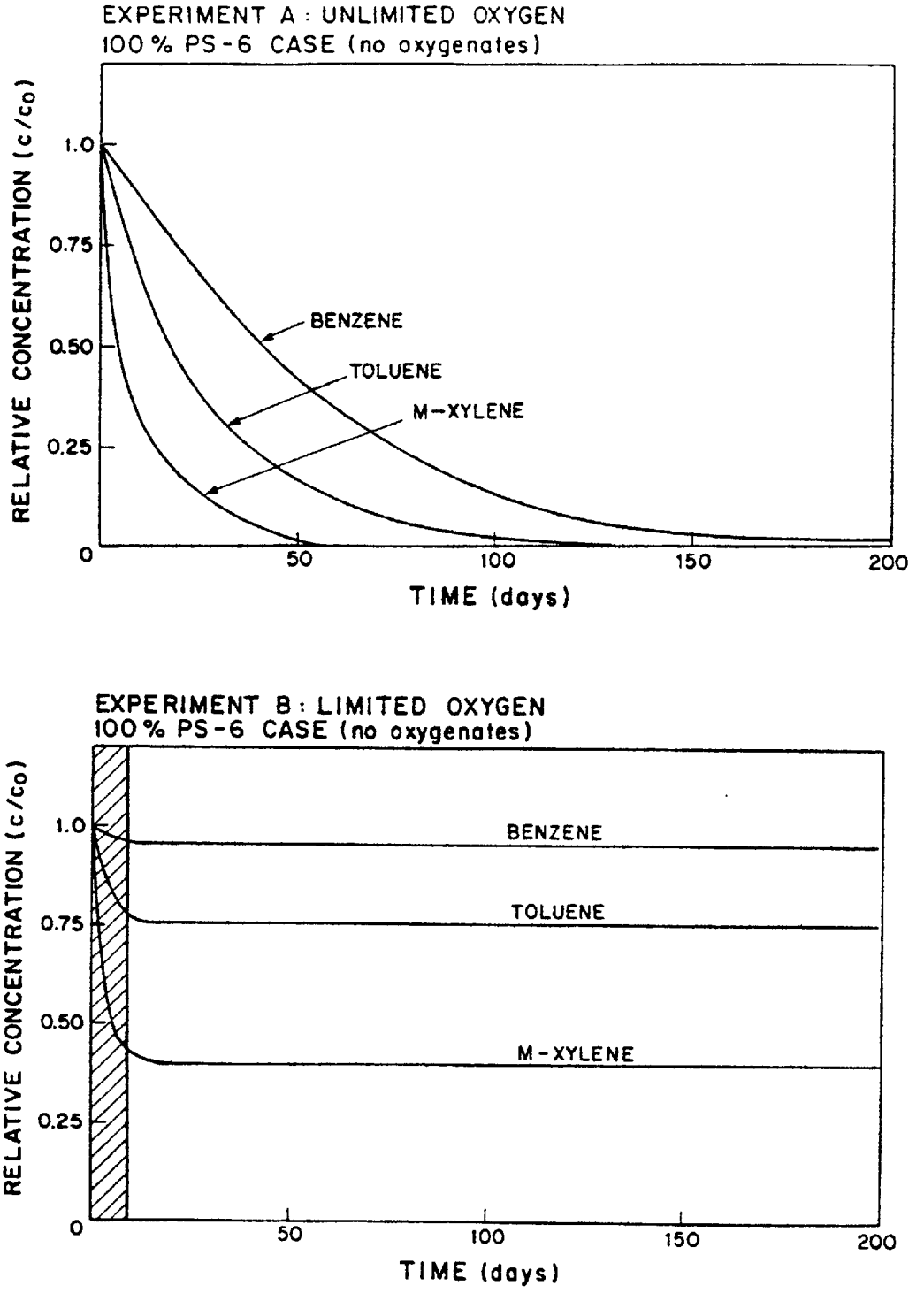


Figure 8-1. Conceptual illustration of relative concentration vs. time for benzene, toluene, and m-xylene in microcosms containing Borden aquifer material and groundwater contacted by 100% PS-6 gasoline. (a) unlimited oxygen case; and (b) limited oxygen case.

metabolizable aliphatic hydrocarbons constitute a large fraction of the total organic carbon in PS-6 gasoline-contacted groundwater (Brookman *et al.*, 1985) and these represent a likely source of the oxygen demand.

The microbial population in the limited oxygen microcosms was unable to transform a measurable quantity of benzene before oxygen was depleted in the microcosms, so benzene persisted at the initial concentration throughout the fifteen-month study. It has been hypothesized that benzene ring cleavage may be particularly difficult for certain microbes to achieve because there are no methyl groups present to disrupt the electron symmetry of the ring (Gibson and Subramanian, 1984). These results lend support to this theory.

In contrast, toluene and m-xylene appear to have been favored by the microbes. Biotransformation of these two compounds was rapid during the aerobic period, accounting for over 70% of the total mass loss observed for the monaromatics. Thus, the early susceptibility of the monoaromatic compounds to microbial attack appears to have strongly influenced their level of persistence in the oxygen-limited microcosms.

8.4 Persistence and Impact of MTBE

In both the unlimited oxygen and limited oxygen experiments, MTBE was recalcitrant over incubation periods of eight to fifteen months. As an example, Figure 8-2 shows a concentration vs. time plot for MTBE in the unlimited oxygen case. Several authors have reported that the ether bond is resistent to microbial attack (Harada and Nagashima, 1975). Jensen (1989) conducted microcosm studies using a mineral-rich medium and a variety of inocula including Borden sand and waste treatment sludge, and saw no MTBE degradation in a series of 60-day experiments. Thomas *et al.* (1988) provided limited evidence of minor biotransformation of MTBE in oxygen-limited microcosms after four weeks of incubation. Experiments of longer duration have not been reported.

MTBE appears to have had little influence on BTEX persistence in the microcosms. Regardless of oxygen availability, biotransformation of the monoaromatics in the presence of MTBE was similar to that in the baseline case with no oxygenates. Minor deviations included less tailing of the mass loss curves for the substituted monoaromatics when oxygen was unlimited, and slightly greater mass losses for these compounds in the limited-oxygen experiments.

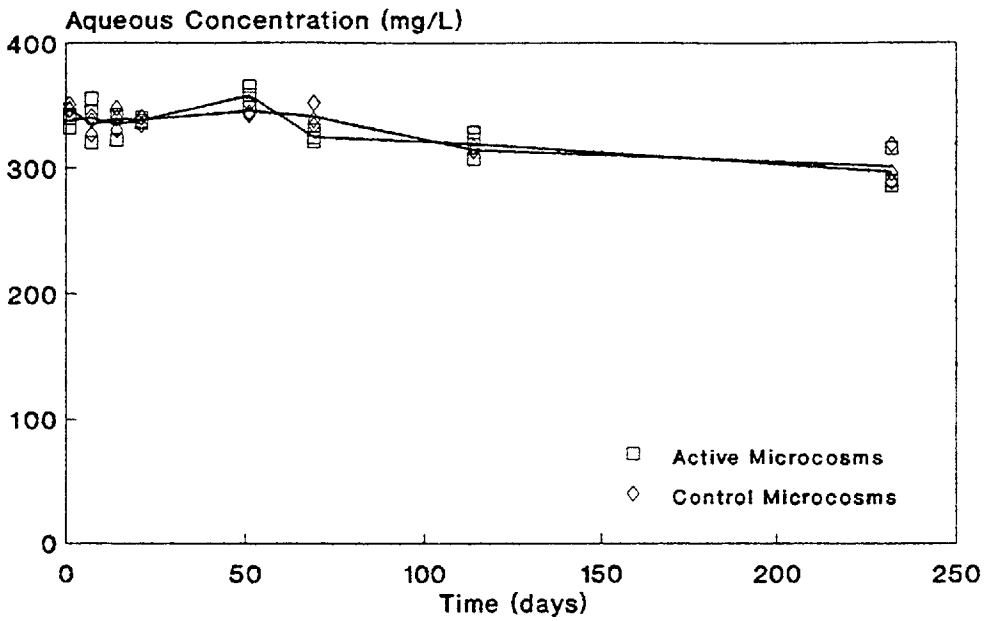


Figure 8-2. Persistence of MTBE in unlimited oxygen microcosms.

8.5 Persistence and Impact of Methanol

Like MTBE, methanol was relatively recalcitrant in both the unlimited oxygen and the limited oxygen experiments. However, there appeared to be some evidence of both aerobic and anaerobic methanol biotransformation following acclimation periods of at least 100 days. As a percentage of the initial concentrations, the methanol losses were small, but they were substantial in terms of mass. Figure 8-3 shows an example of a methanol concentration vs. time plot for unlimited oxygen microcosms. Since methanol biotransformation was only evident by the final sampling session of most of the experiments, tests of longer duration should be conducted to verify this finding and to explore the long term fate of this compound.

Apparent anaerobic biotransformation of methanol coincided with formation of a black precipitate in the hypovials, indicating that sulphate reducers had become active. In anoxic microcosms with no oxygenates, no black precipitate was observed. Although sulphate reducing bacteria are strict anaerobes, and their growth is inhibited in the presence of oxygen, sulphate reduction has been reported in aerobic soils (Grant and Long, 1981), suggesting that the sulphate reducers can survive in aerobic systems. Methanol is biodegradable by sulphate reduction (Braun and Stolp, 1985), so once oxygen was depleted in the microcosms, methanol may have become a metabolizable substrate for the Borden sulphate reducers.

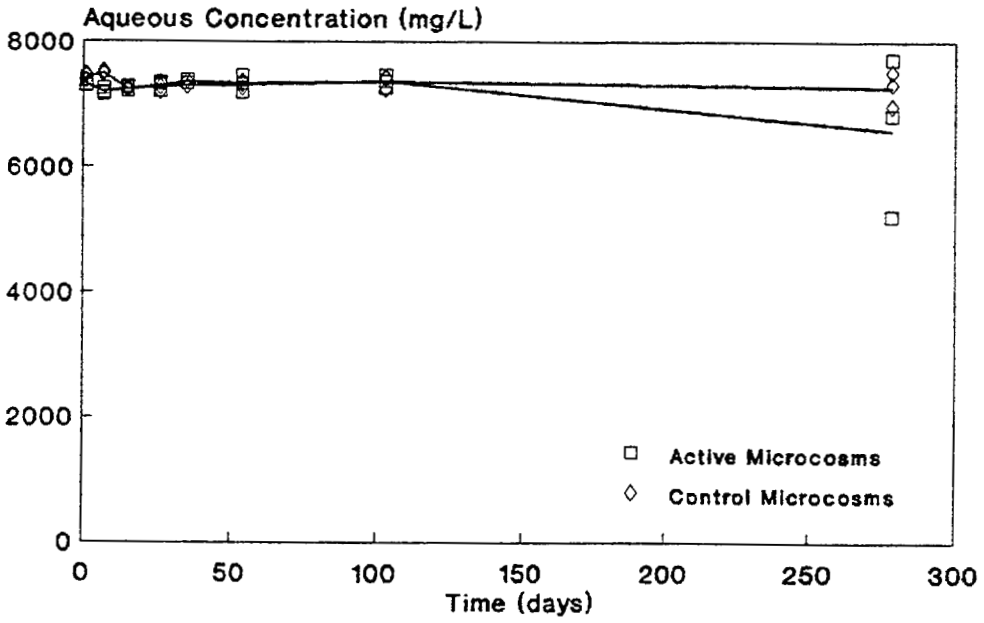


Figure 8-3. Persistence of methanol in unlimited oxygen microcosms.

Hickman and Novak (1989) reported similar findings: methanol biotransformation followed an acclimation period of greater than 100 days in static, limited-oxygen microcosms incubated at 10°C. White (1986) reported complete biotransformation of 1,000 mg/L methanol within one year at a 10°C incubation temperature in limited oxygen microcosms. White observed both the formation of a black precipitate and production of methane, and attributed the methanol biotransformation in his study to a combination of sulphate reduction and fermentation.

Under unlimited oxygen conditions, the influence of methanol on biotransformation of the monoaromatics depended on the initial concentration of methanol. Data from the 85% methanol microcosms provided strong evidence that high concentrations of methanol (7,000 mg/L) can significantly increase the persistence of BTEX. The acclimation periods for the substituted monoaromatics were extended by eight to fifteen weeks, and the subsequent biotransformation rates were dramatically reduced relative to the baseline case with no oxygenates. No biotransformation of benzene was observed over a 10-month incubation period, indicating substantial inhibition of the benzene degraders under conditions of unlimited oxygen availability.

The extension of the BTEX acclimation periods may have resulted from inhibitory effects of the methanol: Ingram and Buttke (1984) report that alcohols can kill bacteria by disrupting the cellular permeability barrier. If portions of the Borden microbial population were killed off or metabolically inhibited by the methanol, the long acclimation periods can be viewed as extended "recovery" periods, after which the microbes are again capable of degrading BTEX. Alternatively, the microbes may have been preferentially transforming methanol at a rate that was below detection. Regardless of the mechanism of inhibition, the results indicate that BTEX persistence may be prolonged on the order of years in the presence of high methanol levels, even when oxygen is plentiful.

At lower methanol concentrations (1,000 mg/L), the biodegradation rates of toluene, ethylbenzene, and the xylenes were slightly enhanced compared to the control case with no oxygenates. Toluene and ethylbenzene acclimation periods increased by about a week, but their overall persistence was slightly shorter than in the baseline microcosms due to the increased rates of biotransformation. In contrast, the benzene acclimation period increased by three weeks relative to the baseline case, and the subsequent biotransformation rate was slow. Benzene biotransformation ceased completely during the latter half of the experiment. Methanol biotransformation may have been occurring preferentially during this period, at a rate that was below the detection limit.

Based on the combined results of the experiments with methanol at 1,000 mg/L and 7,000 mg/L, it can be hypothesized that there is a threshold concentration above which methanol impedes the biotransformation of the substituted monoaromatics and below which the biotransformation of these compounds is enhanced. The effects of methanol on benzene persistence are also concentration-dependent, although at both methanol levels benzene biotransformation was inhibited. It would be necessary to conduct further experiments with a variety of methanol concentrations to gain a clearer understanding of the range of potential effects of this compound on the biotransformation of the monoaromatics when oxygen availability is not a limiting factor.

Under limited oxygen conditions, the effects of methanol on BTEX persistence were more significant. As in the 100% PS-6 control case, oxygen in the microcosms was entirely consumed. However, the duration of the aerobic period was longer in the microcosms containing methanol. Oxygen was depleted in the microcosms with 1,000 mg/L methanol in about three weeks, and in those with 7,000 mg/L methanol within about seven weeks.

Insufficient BTEX biotransformation occurred in the microcosms to fully account for the development of anoxia. Other possible sources for the demand include the aliphatic gasoline components, naturally occurring organic matter, or the methanol. The source of oxygen demand is probably not the methanol, since the duration of the aerobic period was longer in microcosms containing methanol than in those with no oxygenates. In fact, the extended aerobic periods provide indirect evidence that methanol was not being transformed aerobically below detection levels during the first several weeks of the experiments. It is probable that the methanol hindered biotransformation of some of the aliphatics, causing the longer aerobic periods.

The eventual depletion of oxygen in the microcosms magnified both the beneficial and the adverse effects of methanol on BTEX transformation. For example, the enhanced rate of aerobic biotransformation for the xylenes in the presence of 1,000 mg/L methanol resulted in a substantial loss of mass for these compounds in the aerobic period of the limited

oxygen experiment. Once conditions became anaerobic, all three xylene isomers persisted, but at significantly lower concentrations than in comparable microcosms with no oxygenates.

Inhibitory effects of the methanol were also magnified under limited oxygen conditions. At 1,000 mg/L, methanol presence caused a one-week increase in acclimation period for toluene. The increase had little bearing on toluene persistence in the unlimited oxygen microcosms because the subsequent rate of biotransformation was rapid. However, under limited oxygen conditions, the one-week acclimation period had greater significance because it was large relative to the duration of the aerobic period. Less toluene mass was consumed during the aerobic period, and the toluene persisted at higher concentrations than in the baseline case with no oxygenates. In the 7,000 mg/L methanol microcosms, no BTEX biotransformation was detected. The increased acclimation periods induced by the methanol extended beyond the seven week aerobic period of the experiment, and no subsequent anaerobic biotransformation was observed.

These findings suggest that small changes in acclimation period induced by methanol presence will have little influence on the long-term persistence of the monoaromatics in settings where oxygen availability is not a constraint. However, small increases in acclimation period, even on the order of days or weeks, are of much greater consequence under limited oxygen conditions. At high methanol concentrations (7,000 mg/L), the combined effects of methanol presence and oxygen limitation serve to significantly constrain BTEX metabolism in the microcosms, causing long-term recalcitrance.

Although caution is advised when translating the results of microcosm experiments into predictions about actual field behavior, the laboratory experiments do, however, describe the potential limits on solute metabolism in the field. The next section interprets field mass losses in light of the laboratory findings.

Section 9
FIELD BIOTRANSFORMATION

The laboratory biotransformation study identified several means by which the persistence of the monoaromatics can be prolonged in Borden soil and groundwater. In particular, it confirmed previous research identifying oxygen availability as a key controlling factor in BTEX biotransformation. It also showed that, depending on concentration, methanol can inhibit biotransformation of the monoaromatics even when oxygen availability is unlimited, and that the combined effects of high concentrations of methanol and limited oxygen availability can severely constrain BTEX metabolism, with benzene biotransformation affected most severely.

This section explores the role of oxygen in the persistence of the monoaromatics and methanol in the Borden aquifer. Using insights gleaned from the laboratory study, it also attempts to identify the processes responsible for the increased persistence of benzene, ethylbenzene, and p-xylene in the 85% methanol plume.

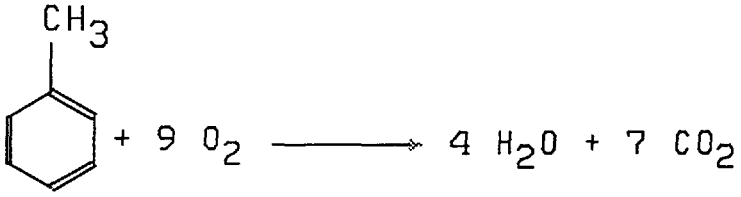
9.1 Oxygen and BTEX Persistence

The availability of oxygen in the plumes of the field experiment was expected to strongly influence the rates of biotransformation of the monoaromatics. The laboratory experiments showed that, in microcosms with a limited oxygen supply, BTEX is readily biotransformed aerobically, but that once anoxia sets in, BTEX biotransformation does not occur at a measurable rate. The limited oxygen microcosms can be considered analogous to the core of a plume, where oxygen cannot be replenished as quickly as it is used for metabolism of BTEX. A correlation should therefore exist between zones of low oxygen and zones of BTEX persistence in the central portions of the field plumes.

Figure 9-1 illustrates the relationship between the distributions of dissolved oxygen and BTEX in the three plumes of this study. It shows a transverse cross section through the three plumes for the fourth sample round. Although the two distributions are not perfectly

comparable because oxygen was measured at 0.4 m intervals while the organics were measured at 0.2 m intervals, the overall patterns are remarkably similar. BTEX is clearly persisting in zones which have become depleted in oxygen. Furthermore, the zone of depleted oxygen is larger for the 85% methanol case, with a correspondingly larger zone and higher concentrations of BTEX. The bimodal concentration distribution observed in longitudinal plume cross sections (Section 5) is also apparent in these transverse cross sections.

The monoaromatics are mineralized in the presence of oxygen according to reactions such as the following for toluene:



Using the stoichiometric relationships of these equations, the oxygen demand exerted by the monoaromatics in the plumes of this study can be calculated. The oxygen mass present in each solute pulse upon injection was about 6-8 grams (Table 7-1). If no other oxygen demand existed in the plumes other than the BTEX, this amount would be sufficient to transform about 5% of the initial BTEX mass. The remainder of the oxygen necessary for BTEX biotransformation could come from diffusion of oxygen at the plume margins, dispersive mixing, primarily at the front and back of the plumes, and advection of oxygen past retarded solutes.

Background oxygen available for entry into the plumes at the depth of the injection zone is shown in longitudinal and transverse cross sections in Section 2, Figures 2-2 and 2-3. Based on these cross sections, it is apparent that background dissolved oxygen in the aquifer carries enough spatial variability that, although it can be averaged for rough estimates of the oxygen available to the plumes for metabolism of the solutes, it will vary depending on location.

Barbaro (1992) has observed that within zones with an initial background concentration of less that 3 mg/L dissolved oxygen, aerobic microbial populations are negligible and significant microbial activity should not be anticipated (see Section 2-4). The longitudinal and transverse profiles given in Figures 2-2 and 2-3 reveal initial background concentrations of 3-4 mg/L, with isolated zones at less than 2 mg/L dissolved oxygen. Based on Barbaro's observations, microbial activity subsequent to injection was probably greatest outside the 2 mg/L contours indicated in Figures 2-2 and 2-3. As a result of biodegradation, dissolved oxygen concentrations dropped to $\leq$ 2 mg/L subsequent to injection, as can be seen in Figure 9-1.

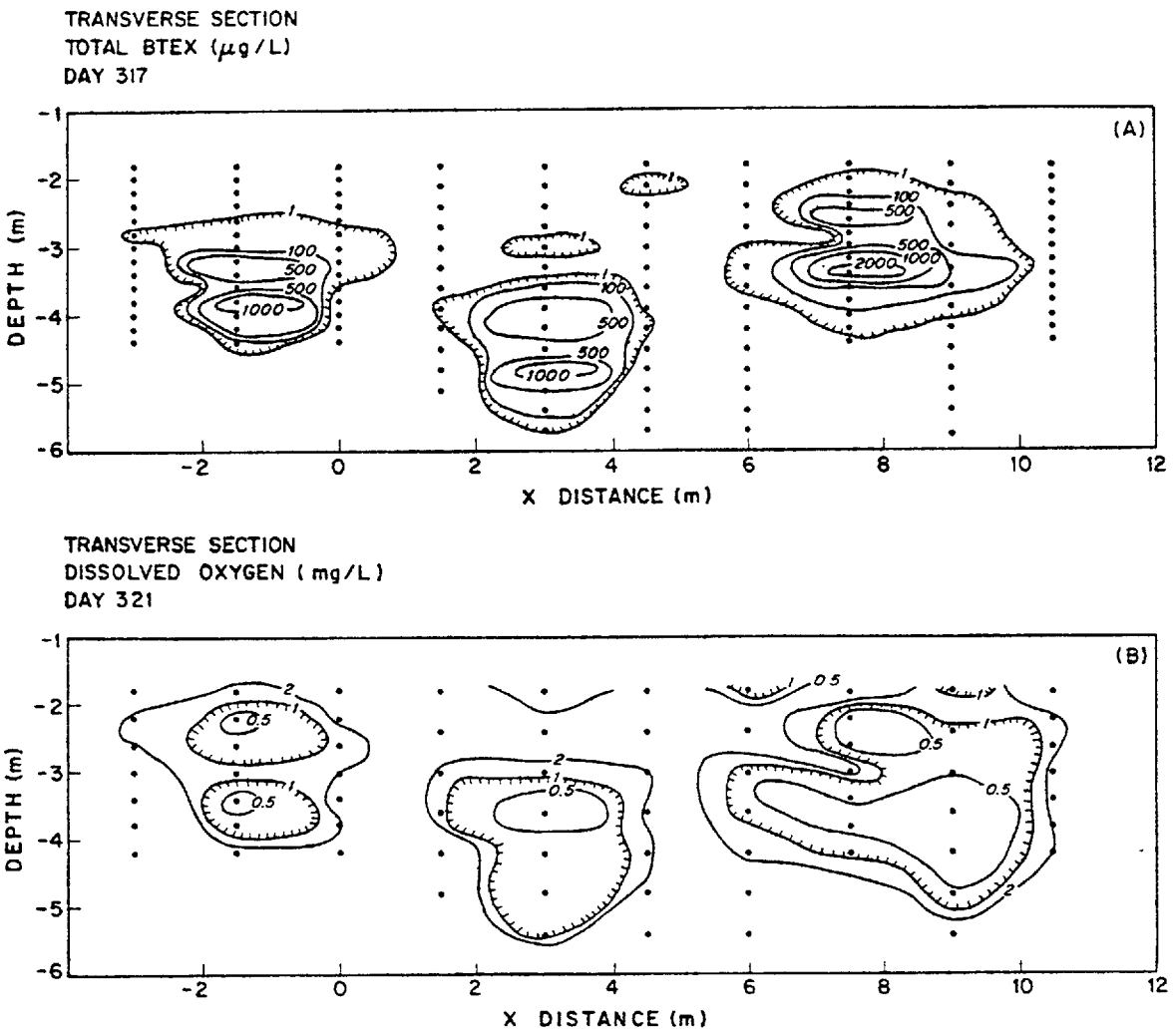


Figure 9-1. BTEX and dissolved oxygen distributions in a transverse cross section through the three plumes at the fourth sample round. Samplers chosen for the section are listed in Appendix F. The 10% MTBE plume is on the left, the 100% PS-6 control is in the center, and the 85% methanol plume is on the right.

The figures show a steeper concentration gradient at the top and bottom of the injection zone than in the lateral direction, so the mass flux of oxygen to the plumes by diffusion will be greater along the top and bottom of the plumes than along the sides. In addition, oxygen advecting in at the back end of the plumes and entering the plumes through dispersive mixing will be available at only 4 mg/L, while higher concentrations (6-7 mg/L) are available above and below the plumes.

In contrast to a single substrate plume, in which advection and longitudinal dispersion can account for significant oxygen entry, the chromatographic separation of the multiple constituents of gasoline plumes, many of which will be degrading aerobically, serves to limit the availability of oxygen in the longitudinal direction. Readily metabolizable substrates such as the aliphatics, many of which are more highly retarded than the xylenes, may exert an oxygen demand behind the xylene plumes, reducing the oxygen available from advection, while biotransformation of the xylenes depletes oxygen behind more mobile solute plumes such as benzene and toluene. Oxygen travels conservatively, so zones of low dissolved oxygen will sweep beyond the retarded monoaromatics, reducing the oxygen levels available by dispersive mixing at the front of the plumes.

The natural distribution of dissolved oxygen in the upper Borden aquifer and the effects of transport and biotransformation of multiple plume constituents combine to make the capacity for oxygen entry greatest through vertical transverse dispersion. If transverse dispersion is the most important mechanism for transport of oxygen into the plumes, dramatic differences in oxygen availability, and therefore, mass loss rates, would not be expected for monoaromatic solutes with different retardation factors.

Equal entry of oxygen into the plumes was invoked by Patrick *et al.* (1986) to explain equivalent rates of mass loss observed for the monoaromatics in a previous Borden tracer test using pure BTEX. Berry-Spark *et al.* (1987) injected and monitored a pulse of gasoline-contacted groundwater, and observed rates that matched those of Patrick *et al.* The experiment of Berry-Spark *et al.* can be compared to the control case of this study,

since they also tracked gasoline-derived monoaromatics. Their experiment differed from this study only in that the initial concentrations of the monoaromatics were considerably lower (by 90-95%). Input parameters for the two studies are compared in Table 9-1.

Table 9-1. Comparison of Initial Conditions for the Natural Gradient Tests of Berry-Spark *et al.* (1987) and this Study.

Parameter	Berry-Spark *et al.* (1987)	100% PS-6 control
Total BTEX (mg/L)	0.7	20.4
Volume Injected, L	2,500	2,835
Average D.O. Conc., mg/L	2.3	2.6
Average Water Temp.	15	18
Injection Date	June 1986	July 1988

In Berry-Spark's experiment, rates of mass loss were several times higher than those of this study for all of the compounds (Table 9-2). This difference can be attributed to the lower initial concentrations of the compounds in the Berry-Spark plume. MacQuarrie *et al.* (1990) simulated the transport and biotransformation of a single monoaromatic at the Borden test site. Concentration was isolated as a variable and simulations were run at several substrate concentrations, holding all kinetic parameters constant. Mass losses were found to be more rapid for lower initial concentrations. MacQuarrie *et al.* (1990) attributed the difference in mass loss rates to the greater oxygen demand of plumes with higher initial concentrations. Rapid oxygen consumption limits biotransformation in these plumes, while biotransformation proceeds unimpeded in the plumes with lower initial concentrations because oxygen availability is not a constraint on solute metabolism.

The concentration of BTEX was so low in Berry-Spark *et al.*'s experiment that sufficient oxygen was available in the solute pulse to serve as an electron acceptor for biotransformation of 85% of the BTEX mass. Discounting other sources of oxygen demand in the plumes, oxygen entry had to account for only 15% of the BTEX mass loss. In contrast, oxygen entry had to account for 95% of the oxygen demand exerted by BTEX

in the control plume of this study. Berry-Spark *et al.*'s experiment can therefore be seen as a system in which oxygen is a relatively unimportant limiting factor, while oxygen availability is significantly limited in the plumes of this study.

As seen in the laboratory study (Section 8), unlimited oxygen systems show only minor differences in relative rates of BTEX biotransformation, while oxygen-limited systems show more dramatic differences in BTEX biotransformation rates. In the limited oxygen case, more mass loss occurs during the initial anaerobic period for compounds that are especially susceptible to microbial attack than for compounds that exhibit an early recalcitrance. In the oxygen-limited laboratory experiments, toluene and m-xylene had particularly rapid early mass losses, while benzene was recalcitrant at early times. In the field, differences in the rates of mass loss for toluene and m-xylene and benzene were observed in the control plume of this study (oxygen-limited system), but not in that of Berry-Spark et al. (oxygen essentially unlimited).

Table 9-2 shows mass loss rates for the control plume of this study, for the control plume of Berry-Spark *et al.*, and for the laboratory biotransformation experiment with no oxygenates added and unlimited oxygen availability. The rates for the laboratory experiment with unlimited oxygen nearly match field rates observed by Berry-Spark, adding support to the hypothesis that their system was not severely constrained by limited oxygen availability. In contrast, the biotransformation rates of this study were slower, and there were clear differences in rates of mass loss for the compounds.

These findings indicate that the condition observed in the laboratory, in which the persistence of the compounds in an oxygen-limited setting depended on their early susceptibility to microbial attack, bears out in the field. The differences in mass loss rates observed for the monoaromatics in this field experiment are probably not related to differences in oxygen entry into the individual solute plumes. Instead, the relationship between the initial substrate concentrations and the availability of dissolved oxygen for the entire gasoline plume establishes the chemistry of the system (oxygen limited vs. oxygen

Table 9-2. Comparison of First Order Mass Loss Rates (day^{-1}).

Solute	Berry-Spark *et al.* (1987)	100% PS-6 Control This Study (Lab)	100% PS-6 Control This Study (Field)
Benzene	0.019	0.024	0.004
Toluene	0.024	0.037	0.013
Ethylbenzene	0.024	0.031	0.008
p-Xylene	0.023	0.025	0.007
m-Xylene	0.034	0.038	0.010
0-Xylene	0.019	0.030	0.006

unlimited), and some solutes are favored for metabolism over others when, as in this study, oxygen availability is limited. For gasoline plumes in which concentrations are low enough and oxygen levels are high enough that oxygen is not a limiting factor, biotransformation rates are relatively uniform for the monoaromatics and can be predicted using static laboratory microcosms.

9.2 Oxygen and Methanol Persistence

The laboratory study did not provide strong evidence of either aerobic or anaerobic biotransformation of methanol. Both appear to have occurred, but only after initial lag periods of 100 days, and then at very slow rates. In contrast, field mass loss rates for methanol were extremely rapid following an initial 100-day lag period. It is possible that some key nutrient necessary for methanol transformation was depleted in the microcosms but was not limited in the field where transport processes permit access to more nutrients. Alternatively, the microcosms may not have contained a sufficiently diverse representation of the microbial population to include a robust group of methanol degraders.

In order to determine whether the observed removal of 99.9% of the methanol mass in the field experiment occurred by aerobic or anaerobic biotransformation, a mass balance can be performed. The reaction for the aerobic mineralization of methanol can be written as:

$$CH_3OH + 3/2\ O_2 \longrightarrow 2\ H_2O + CO_2$$

Based on the stoichiometry of the equation, about 1.4 grams of oxygen are required for mineralization of each gram of methanol. If the initial mass of methanol is taken to be about 14,000 grams (average of the mass estimates for the first three sample rounds), nearly 19,600 grams of oxygen would be required to account for the observed depletion of the methanol mass. If the methanol were not entirely mineralized, and the reaction proceeded only to the formation of formaldehyde (the intermediate breakdown product), 14,000 grams of oxygen would be required for aerobic transformation of the methanol.

The oxygen mass available for methanol biotransformation includes that which was present in the injected pulse (about 8.7 g), and that which entered the plume from background groundwater over the course of the experiment. A nonsorbing solute such as methanol will receive oxygen by diffusion at the plume boundaries and through mechanical dispersion: it will not receive oxygen by advection. If the methanol plume were not biodegrading, the mass of oxygen entering the realm of the methanol plume by dispersion could be estimated by calculating the change in volume of the methanol plume over time and assuming an average value of background dissolved oxygen available for plume entry. However, since the methanol plume was rapidly biotransformed, changes in its size over time were not a reflection of dispersion. As an alternative, the change in volume occupied by the conservative tracer, chloride, which did not undergo any chemical transformation but traveled at the same rate as the methanol, can be used in the calculation.

Figure 9-2 shows a plot of cumulative oxygen entry into the methanol plume. The dissolved oxygen mass available for transformation of the methanol was approximated by assuming that the change in liquid volume occupied by the chloride plume through time was equivalent to the volume of water containing background levels of oxygen that entered the realm of the methanol plume. Background oxygen was assumed to average 4 mg/L. Estimates of the change in plume volume were made by measuring the length, width, and depth of the chloride plumes at each sample event and assuming an elliptical shape in plan view and a uniform plume thickness at each sample event.

Discounting other sources of oxygen demand, cumulative oxygen entry (Figure 9-2) can be added to the mass of oxygen in the injection solution to obtain an estimate of 432 g for the maximum possible mass of oxygen available for aerobic methanol transformation by the end of the experiment. This represents only 2% of the oxygen mass that would have been required to mineralize the methanol aerobically, so anaerobic biotransformation, must be invoked to account for the observed methanol loss.

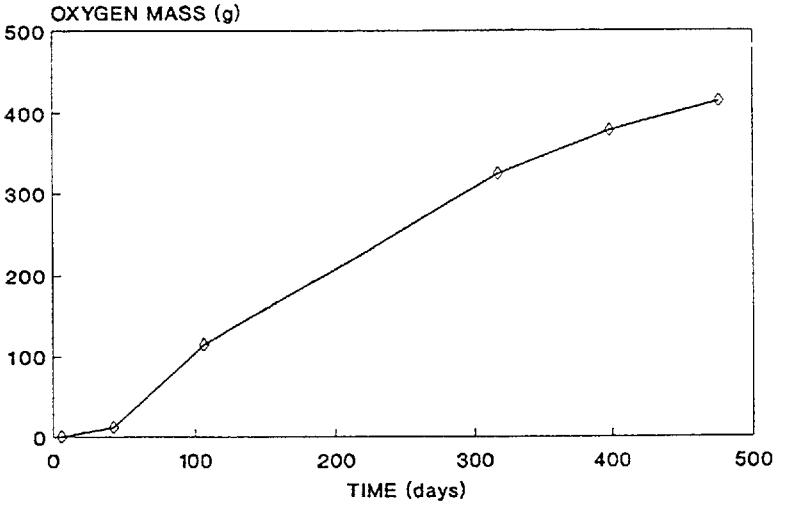


Figure 9-2. Cumulative oxygen entry into the methanol plume.

One way to determine whether methanol was biotransformed aerobically in the field at all, or whether the entire process was anaerobic, is to examine the profiles of dissolved oxygen in the 85% methanol plume and the 100% PS-6 control plume. If methanol did not undergo aerobic biotransformation, the profiles should essentially match. Figures 9-3 and 9-4 show dissolved oxygen profiles for the 85% methanol case and the control case on Days 106 and 317. On Day 106, no measurable biotransformation of methanol had occurred. By Day 317, nearly 75% of the methanol mass had been removed.

Examination of the profiles shows that, on Day 106, the dissolved oxygen in the two cases did not differ substantially (Figure 9-3). However, by Day 317, the 85% methanol plume

contained significantly less oxygen than the control case. The zone of depressed oxygen in the 85% methanol plume (including a large proportion that had gone completely anaerobic) resided at the front of the monitoring network where the methanol is located, while the oxygen distribution at the back of the plume (where the xylenes resided) was comparable to that of the control (Figure 9-4).

This suggests that aerobic biotransformation of methanol did not occur prior to Day 106, but that methanol was biotransformed aerobically following the third sample event. Once oxygen had become depleted in the core of the plume, anaerobic microbial populations may have been favored, and a shift to anaerobic methanol transformation became possible. Evidence of a shift to anaerobic microbial populations was observed in the laboratory experiments in the form of increased activity of the sulphate reducers following the development of anoxia in the microcosms.

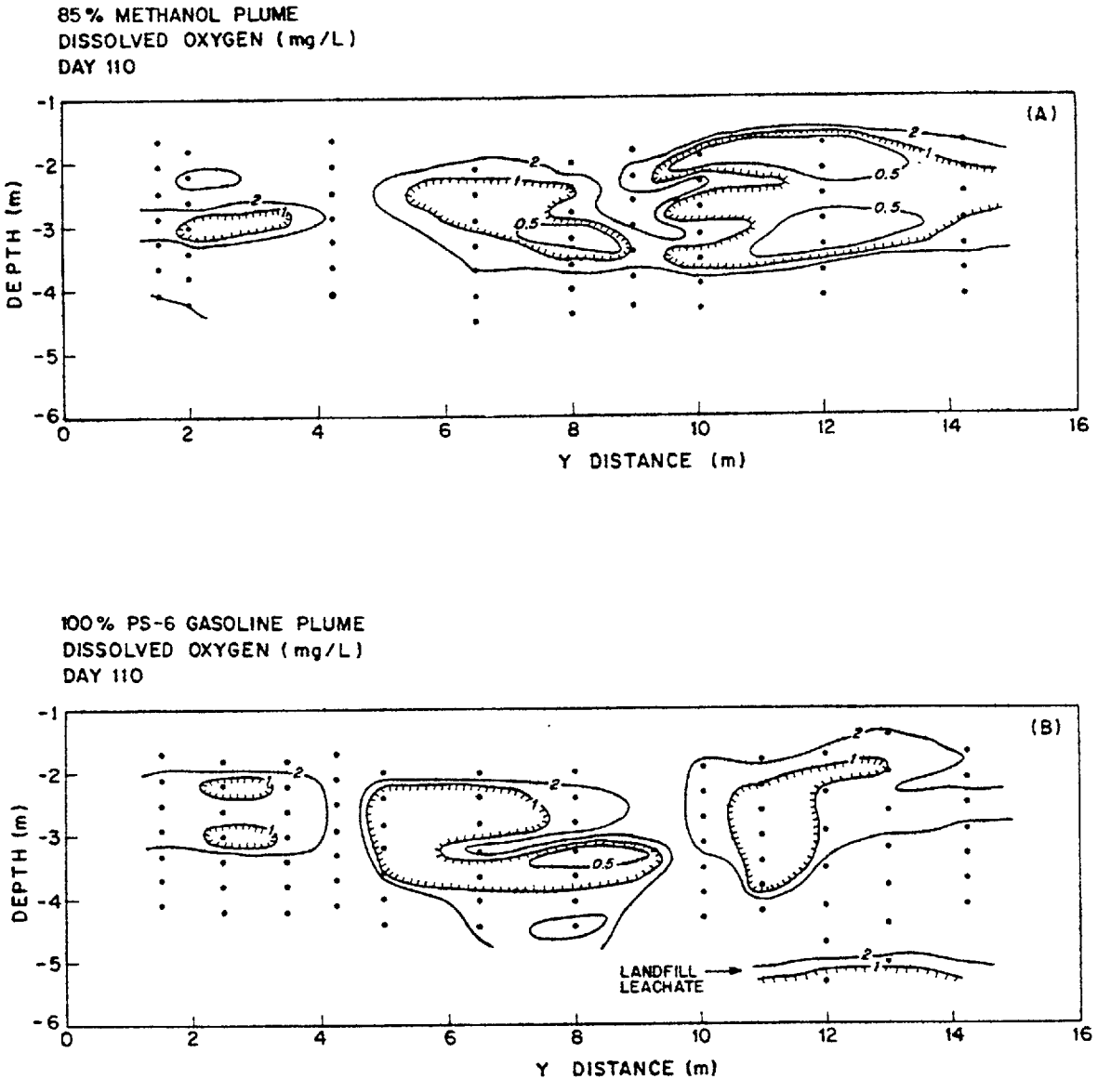


Figure 9-3. Dissolved oxygen along the plume centerline: Day 106. (a) 85% methanol case and (b) 100% PS-6 gasoline control case.

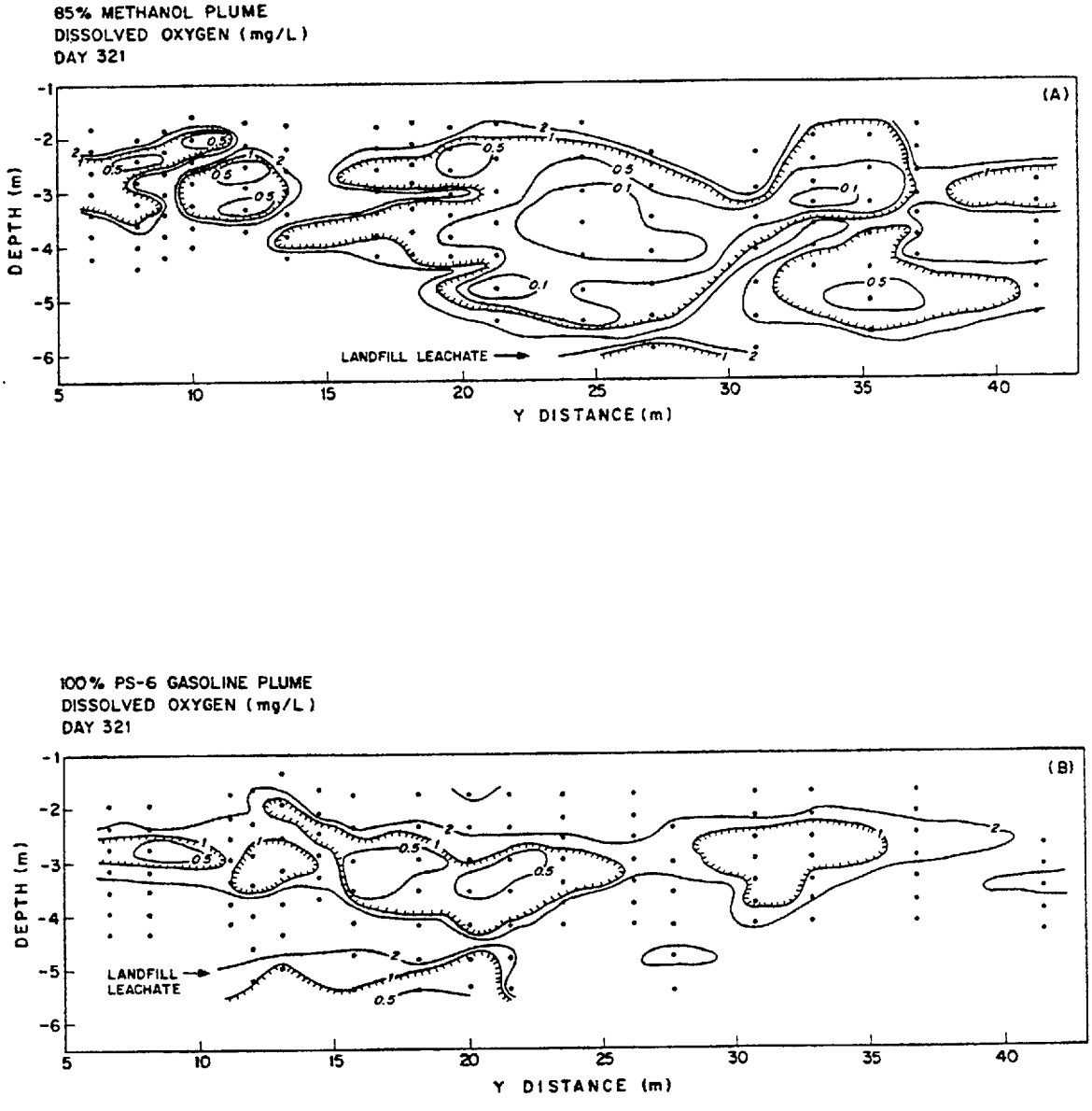
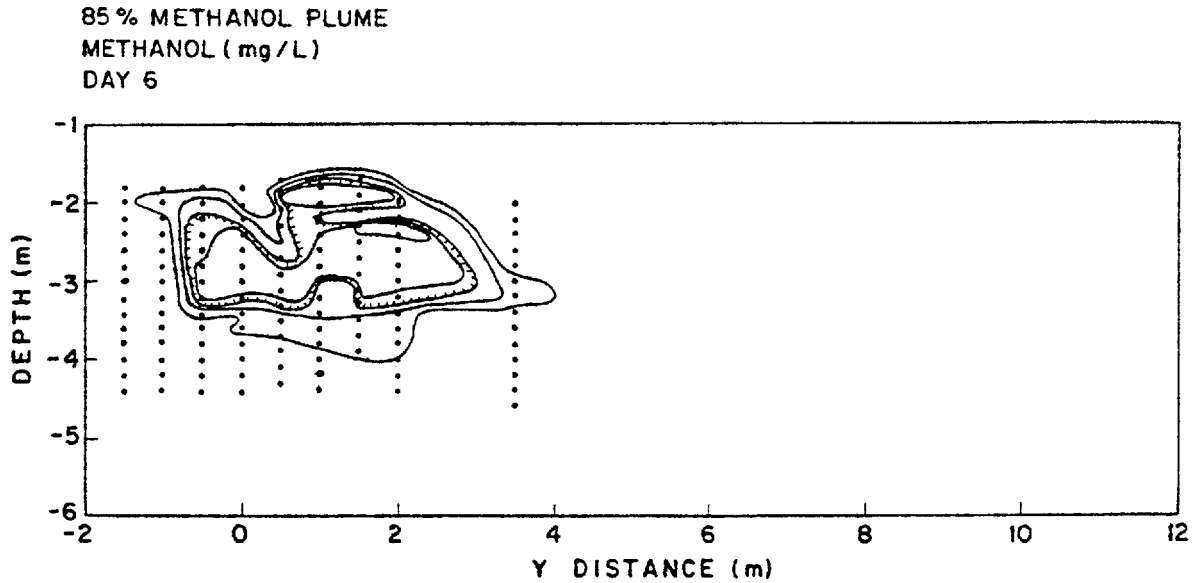


Figure 9-4. Dissolved oxygen along the plume centerline: Day 317. (a) 85% methanol case and (b) 100% PS-6 gasoline control case.

If no aerobic biotransformation occurred in the field during the 100-day lag period, then it can be assumed that methanol mass was conserved during this period, and that the delayed onset of biotransformation represented a true acclimation period for the subsurface microbes. Such a lag period was also observed in the laboratory: in static microcosms, no measurable methanol loss occurred for 100 days, and no depletion of oxygen attributable to methanol loss occurred during this period.

This apparent consistency of lag period duration for the field and the laboratory may be fortuitous. For example, in the case of the methanol plume of this study, the average velocity of its center of mass is about 9 cm per day, so the plume must become at least 9 meters long for the microbes, which are generally attached and not mobile, at its back end to have the 100-day contact time necessary for acclimation. An examination of the cross section for methanol on Day 106 (Figure 9-5) indicates that, by this sample event, the upper and lower portions of the plume have just about reached this size, and that the microbes in the back portions of the plume may have had sufficient contact time with the methanol to acclimate. Prior to this sample event, the plume is too small to permit the needed contact time. Based on this observation, it appears that the similarity of lag periods observed in the field and the laboratory may result from different processes: the laboratory lag period can be attributed strictly to microbial acclimation, while the field lag may represent the amount of time it takes for a microbial population within the domain of the plume to have sufficient contact time for acclimation.

Based on this view of acclimation in a dynamic system, we would also expect the mass loss for methanol to be most dramatic at the back end of the plume. A review of Figure 5-8, which shows a cross section of methanol and chloride in the fourth sample round indicates that, in keeping with this hypothesis, the majority of the methanol transformation has occurred at the back of the plume.



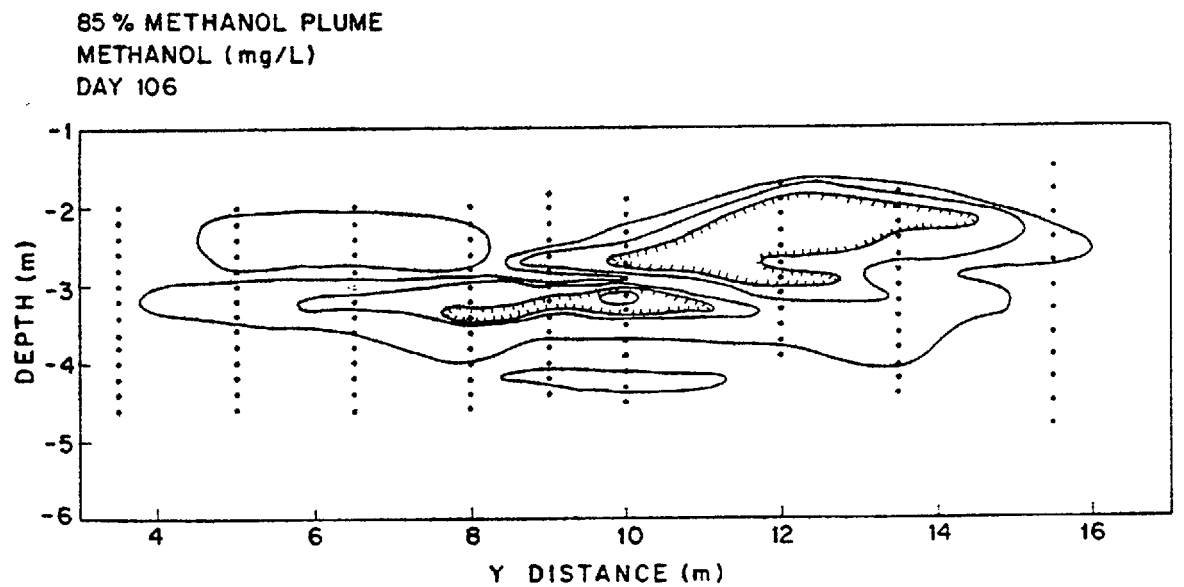


Figure 9-5. Methanol distributions along the plume centerline on Day 6 and Day 106. Values of the contour lines are 1, 1,000, 3,000, 5,000, and 7,000 mg/L. The 3,000 mg/L line is highlighted.

9.3 Impact of Methanol on BTEX Persistence

Benzene biotransformation was significantly inhibited in the 85% methanol plume. The laboratory biotransformation experiments provided some insight into the mechanisms that may have been responsible for this inhibition. In the laboratory, under conditions of unlimited oxygen, methanol at 7,000 mg/L was seen to entirely inhibit benzene biotransformation, while benzene biotransformation was merely slowed in the presence of 1,000 mg/L methanol. Since oxygen was fully available, the inhibition of benzene biotransformation in the microcosms was likely the result of inhibitory effects of the high methanol concentrations on the benzene degraders. The inhibition of various methanol concentrations upon Borden aquifer microbes is currently underway.

High methanol concentrations were present in the 85% methanol plume through Day 106, prior to the onset of methanol biotransformation. Figure 9-5 shows the methanol distribution on Days 6 and 106, with the 3,000 mg/L contour highlighted. By Day 106, although concentrations were reduced relative to the initial condition due to dispersion, portions of the plume retained methanol concentrations in the thousands of milligrams per liter. Furthermore, at the Day 106 sample event, the benzene and methanol plumes had not yet separated substantially in space.

Growth or cell function of the microbial populations capable of degrading benzene may have been inhibited in the zones of high methanol, while transformation of benzene continued unimpeded on the plume margins. This process could account for the slower rate of loss for benzene in the 85% methanol plume relative to the control for the first 106 days of the study. Following Day 106, methanol was rapidly transformed, and concentrations dropped significantly, reducing the inhibitory capacity of the methanol itself. However, if methanol were incompletely oxidized and the reaction proceeded only to formaldehyde, this breakdown product could inhibit microbial populations as well.
Formaldehyde is used as a sterilent at concentrations as low as 250 mg/L. Concentrations of formaldehyde in the plumes would also reduce with time due to dispersion.

The methanol traveled ahead of the benzene plume, so the amount of inhibition of benzene mass loss would have depended in part on the time needed for recovery by impaired microbial populations. The methanol and the benzene plumes became more and more separated in space over the course of the experiment, so inhibitory effects of the methanol or its breakdown products probably became a less significant mechanism for reduced rates of benzene biotransformation with time.

As discussed in the previous section, the rapid loss of methanol corresponded to the development of oxygen-depleted zones in the core of the methanol plume. At any location where benzene was also present in these zones, benzene biotransformation would have been entirely inhibited, yet benzene transformation could have continued on the plume margins where oxygen was continuously available. Since the two mechanisms of inhibition --

(1) inhibitory effects of the high methanol levels (or, potentially, formaldehyde levels) on the microbial population; and
(2) depletion of oxygen due to aerobic transformation of methanol

would have occurred in similar regions of the benzene plume (i.e., zones in the plume core) there is no reason to expect to see changes in the benzene mass loss curve corresponding to a change in the mechanism of inhibition. The two mechanisms could have been in effect at two different times in the experiment, or operating at different locations within the plume, and the benzene mass loss curve would still exhibit a gradual decline.

p-Xylene and ethylbenzene biotransformation was inhibited to a lesser extent in the 85% methanol plume. In the unlimited oxygen laboratory experiment, transformation of these compounds was inhibited only by the highest concentration of methanol tested (7,000 mg/L). Thus, any inhibitory effects of the methanol on the microbes that degrade these compounds would have been limited to smaller zones and to earlier times than for the benzene plume. In addition, after Day 106 the xylenes became separated from the methanol due to their slower rate of transport, so oxygen depletion beyond that observed for the control did not occur in these plumes. Reasons for the lack of inhibition of o-xylene biotransformation in the 85% methanol plume are not clear since this compound exhibited identical behavior to p-

xylene and ethylbenzene in all other respects. Possibly the effect is masked by the error associated with estimation of the plume mass.

In general, toluene and m-xylene were most susceptible to microbial attack in the laboratory experiments and were least affected by methanol presence. However, their biotransformation was inhibited in the presence of 7,000 mg/L methanol in laboratory microcosms. It is possible that, in the field, the biotransformation of these compounds on the plume margins was sufficient to override any reductions in their biotransformation rate in core zones of high methanol.

9.4 Comments on Field Biotransformation Findings

The field observations of solute mass loss indicate that, with time, the more severe constraints on metabolism of the monoaromatics predicted by the laboratory study are mitigated in the field by transport processes. Even when the constraints on metabolism induced by high methanol levels or depletion of oxygen are operating in zones of the plume core, biotransformation can continue on the plume margins, so no complete inhibition of mass loss is observed in the field.

The inhibitory effects of methanol on microbial populations within the plume core are lessened as methanol concentrations drop due to dispersion and biotransformation, and core zones of high methanol become smaller with time. The constraint on metabolism imposed by oxygen depletion due to methanol biotransformation affects only the very mobile benzene plume in the field, because the more retarded monoaromatics plumes are separated from the methanol plume before the methanol biotransformation begins.

The effectiveness of many of these mitigating factors is expected to be a direct consequence of the form of the contaminant release. For continuous sources of groundwater contamination by gasoline constituents, such as floating pools of gasoline at the water table, solute transport phenomena would provide fewer benefits than those observed for the pulse input of this study.

Section 10
CONCLUSIONS AND IMPLICATIONS

This section summarizes the conclusions of the study and briefly comments on practical implications of some of the findings for site investigation and environmental policy.

10.1 General Solute Flow

The chloride plumes for the three test cases traveled side by side, with minimal lateral overlap, at an average velocity of about 9 cm per day, and, as expected, their mass did not change with time. They elongated in the direction of groundwater flow, expanding to five times their original length over the sixteen month experiment. Little spreading occurred in the horizontal and vertical transverse directions. Longitudinal and transverse dispersivity estimates were similar for the three plumes, indicating they encountered the same degree of aquifer heterogeneity along their travel paths. This equivalence of movement for the three chloride plumes was essential to the study's objectives, in that hydrogeological parameters could be ruled out as experimental variables and differences in mass loss rates for the organic solutes could be attributed solely to geochemical factors.

10.2 Transport of the Organic Solutes

Methanol and MTBE traveled at the same rate as the conservative tracer, while the monoaromatic hydrocarbons were retarded to varying degrees. Benzene transport was most rapid, with a retardation factor of 1.1, and ethylbenzene and the xylenes traveled at the slowest rate, with a retardation factor of about 1.5. A chromatographic separation of the plumes occurred, and the degree of plume overlap decreased over the course of the experiment. This spatial separation served to reduce the potential for effects of the oxygenates on the monoaromatics with time.

No effects of the oxygenates on the rate of transport of the monoaromatics were distinguishable, even at early times when oxygenate concentrations were at their highest and all of the solutes occupied the same volume of the aquifer. Only when methanol

concentrations exceed 250,000 mg/L would enhanced mobility of BTEX be anticipated. The initial methanol concentration for this study was about 7,000 mg/L. At an accidental spill site, effects of the oxygenates on BTEX mobility cannot be discounted, because the volumes of gasoline spilled are likely to be greater, and near-source concentrations of methanol could easily exceed the 25% level at which significant cosolubility effects are produced.

10.3 Biotransformation of the Monoaromatics

The monoaromatics in the control plume of this study biodegraded at a slower rate than that observed for previous field experiments with gasoline constituents at the Borden site. This slower rate of mass loss is attributable to the higher initial solute concentrations in the plume, which produced a greater oxygen demand and led to the development of anoxic zones in the plume core. Under these oxygen-limited conditions, toluene and m-xylene degraded most rapidly, while benzene degraded more slowly. In contrast, at previous tests at the site, in which the initial concentrations were low and oxygen was a less important limiting factor, biotransformation rates for the monoaromatics were essentially equivalent.

These findings indicate, even for plumes emanating from small spills of gasoline, such as those simulated in this study, concentrations of the monoaromatics are likely to be high enough to exert a significant oxygen demand and produce an oxygen-limited system. In such a system, benzene will be most resistant to biodegradation. Time periods required for reduction of benzene concentrations to drinking water standards by passive *in situ* bioremediation could be extensive. Furthermore, at late times, the biodegrading organic solutes of this study tended to persist at relatively high concentrations in unconnected zones, similar in scale to the aquifer sand beds, on the order of a few meters long and less than a meter thick. Such thin, narrow zones of high concentration could be easily missed in a standard hydrogeological monitoring program. The importance of such zones for water supply will be site specific.

10.4 Fate and Impact of MTBE

MTBE was recalcitrant in both the laboratory and field, and showed no effect on the rates of biotransformation of the monoaromatic hydrocarbons relative to the control. MTBE's recalcitrance may be related to the Borden geochemical setting, although no conclusive evidence of MTBE biotransformation has been reported in the literature.

Regardless of the nature of the recalcitrance, when gasoline containing MTBE is introduced to the groundwater zone, MTBE can be expected to travel at the same rate as the groundwater at the site, and MTBE plumes are likely to undergo only dispersive attenuation. MTBE plumes will rapidly occupy large portions of the subsurface and no natural biological removal of MTBE mass will occur. MTBE should be a useful indicator compound for groundwater contamination from gasoline spills. MTBE fuels will contain proportionally less BTEX than unleaded gasoline and so will release less BTEX per volume of fuel spilled.

10.5 Fate and Impact of Methanol

Methanol biotransformation was observed in both the laboratory and field. In the field, a three and a half month lag period preceded the onset of rapid methanol biotransformation. At the close of the sixteen month experiment, after only about 45 meters of travel in the aquifer, less than one percent of the methanol remained. Oxygen was depleted rapidly in the plume after methanol biotransformation began, but insufficient oxygen was available to account for all of the methanol removal, so methanol is considered to have biodegraded by first aerobic, then anaerobic, mechanisms.

Implications of these findings are that, even at the high methanol concentrations of this study (several thousand mg/L), microbial communities in the subsurface are capable of transforming methanol at a rapid rate, and biotransformation continues even under the changing geochemical conditions of oxygen depletion in the plume core. As a groundwater contaminant, then, methanol can be expected to be passively remediated in a variety of hydrogeological settings. Its breakdown is rapid following initial acclimation

periods, so even though it is nonsorbing and travels conservatively, complete biotransformation can occur over relatively short travel distances.

Although the natural biotransformation of methanol is advantageous in removing methanol mass from the groundwater environment, the resulting changes in the geochemistry of the gasoline plumes can affect the subsurface behavior of other constituents. For example, one potential result of the breakdown of methanol that should be explored is the possible production of formaldehyde, an intermediate breakdown product. This compound is slated for regulation under the U.S. Safe Drinking Water Act and has potential to influence biotransformation rates of the monoaromatics.

Furthermore, this study showed that methanol presence inhibited the natural bioremediation of the monoaromatics, most notably benzene. The combined effects of methanol presence and oxygen depletion entirely prevented BTEX biotransformation in microcosms with a limited oxygen supply. In the field, severe constraints on solute metabolism were mitigated by transport processes for most of the solutes, but the rate of benzene biotransformation was still significantly reduced. For pulse input sources, such as those of this study, spatial separation of the plumes with time, and reductions in methanol concentrations due to dispersion, combine to lessen the impacts of methanol presence on field biotransformation of BTEX.

10.6 Extension of Findings to Other Hydrogeological Settings

The Borden aquifer represents a simple physical and chemical system. Extrapolation of the results of this study to more complex environments would be improved by additional scientific studies to define:

1) the interactions between transport phenomena and chemical factors influencing mass loss rates;

2) the role of formaldehyde as a potential breakdown product and microbial growth inhibitor;

3) the apparent concentration dependence of methanol's effects on biotransformation of the monoaromatics; and

4) the spatial relationships between hydraulic conductivity, groundwater chemistry, and microbial activity (or biotransformation potential for the monoaromatics).

Because of the complex nature of the interactions of solute transport phenomena and the chemical evolution of multiple constituent plumes, extension of many of the findings of this research to different hydrogeological environments would best be accomplished with the assistance of computer models that incorporate the physical and chemical processes and the detailed variability of flow velocity explored in this study.

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APPENDIX A

THE FIELD INJECTION

Contents:

Tables:

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A.1 Design of the Injection System

The solute injection system was designed by Karen Berry-Spark of Beak Consultants, Inc. A schematic diagram of the field apparatus is shown in Figure A-1. The source well was located about 100 meters north of the injection zone. It was constructed of six inch O.D. PVC, with a slotted screen spanning the same depth interval as the injection wells. Two PVC bags, each with a 2,000 L capacity, were used as a groundwater reservoir. A garden hose connected the source well and reservoir, and a gasoline pump was used for groundwater extraction. An electric pump withdrew water from the reservoir at flow rate of 11 liters per minute, and passed it through a polyethylene line to a junction with a Teflon line leading from the gasoline saturator.

The system for saturating water with gasoline consisted of three 45 gallon metal drums. Gasoline was equilibrated with site groundwater in the barrels before the injection. The barrels were fitted with Teflon outlet hoses that permitted withdrawal of the gasoline saturated water from the bottom of the barrel, and prevented extraction of gasoline. A peristaltic pump was used to withdraw water from the barrels at a rate of 1.6 liters per minute. An inline sampling port permitted collection of samples of the gasoline-contacted water prior to dilution with groundwater from the reservoir.

Three metal 45 gallon drums held solutions of chloride and methanol or MTBE. The solutions were withdrawn from the containers through Teflon tubes using a peristaltic pump at a rate of 0.3 liters per minute. Three 20 L glass carboys fitted with rotary blades and located immediately in advance of the injection wells served as mixing vessels for the solutions. Three inline ports permitted withdrawal of water samples for each solution prior to injection.

Patrick (1986) calculated an optimal flow rate of 1.5 L/min for injection of groundwater at this site. This flow rate was also used successfully by Berry-Spark (1987) and was adopted for this experiment. At an injection rate of 1.5 L/min, creation of three 3000 liter solute pulses using nine injection wells was expected to take about eleven hours.

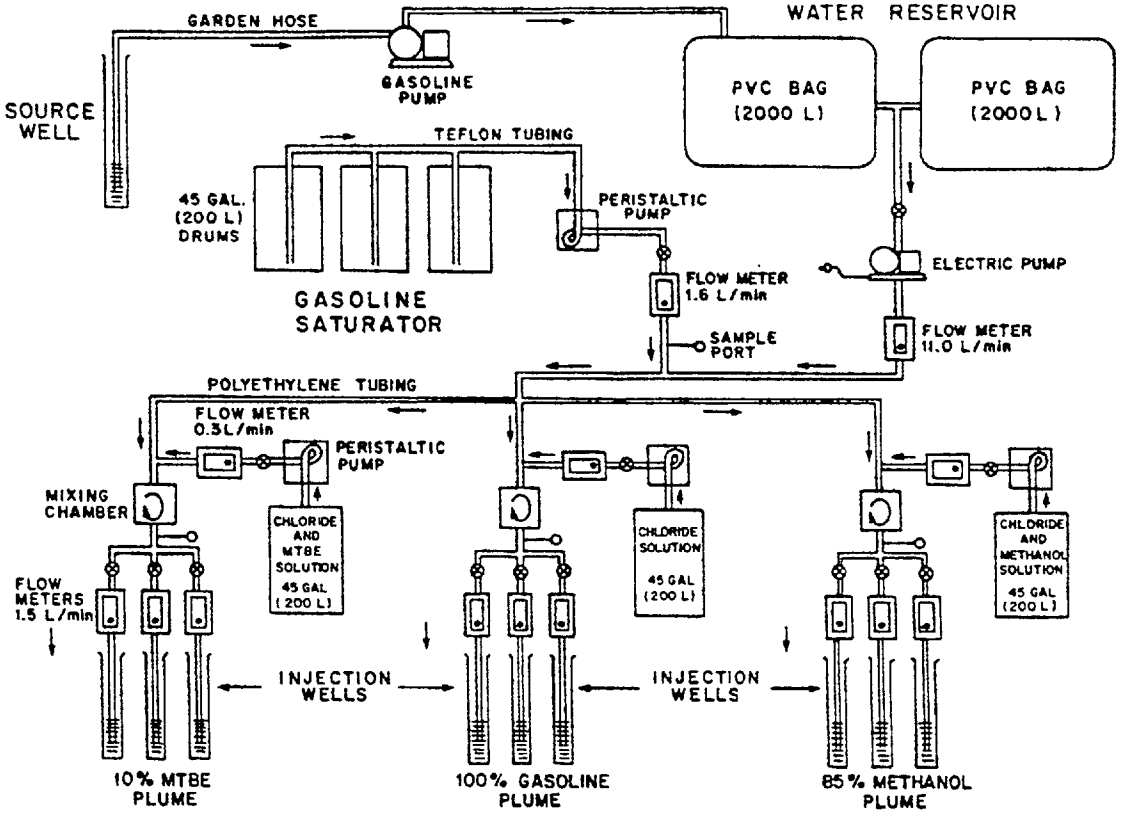


Figure A-1. Schematic diagram of the solute injection system.

The injection wells were constructed of 5.08 cm I.D. PVC pipe fitted with 0.61 meters of threaded No. 10 commercial well screen. The wells were installed during the week of June 20, 1988 by a jetting of casing method (Cherry *et al.* 1983) using a Cobra percussion hammer and onsite groundwater. They were developed by pumping for 5-10 minutes until they yielded clear water.

A.2 Injection of the Solutes

On July 13, 1988, approximately 8.5 cubic meters of solution was injected into the aquifer (about 2835 liters for each plume) over a twelve-hour period. The injection proceeded as follows. Ten liters of PS-6 gasoline was added to each of the gasoline-saturator barrels, and they were filled to within six inches of the top with site groundwater (190 L) and covered. The liquids were stirred for two hours and then the stirrers were removed and the liquids equilibrated undisturbed in the covered barrels for four hours. API (1991) found that PS-6 gasoline:water systems reach equilibrium after about an hour, so four hours was considered sufficient.

The solutions of methanol, MTBE, and chloride were also prepared in advance. Each spike drum was filled with 200 liters of site groundwater and 2.5 kg of sodium chloride. About 1.5 kg of MTBE was added to the drum for the 10% MTBE pulse, and about 18.3 kg of methanol was added to the drum for the 85% methanol pulse. The solutions were mixed for 15 minutes using rotary mixers.

Once equilibrium had been reached in the gasoline saturator, and the chloride and oxygenate spike solutions were mixed, the injection system was activated. Groundwater was withdrawn from the source well and stored in the two reservoirs. Water from the reservoirs was mixed with the gasoline-saturated water at a 10:1 (v/v) ratio. The dilute solution of gasoline constituents flowed into three separate lines. Solutions of sodium chloride and the oxygenates were spiked into the appropriate lines, and the three solutions passed through the mixing vessels and flowed into the injection wells. Control of the input concentrations was achieved by adjusting the relative flow rates of the source and spike lines.

The solutions were injected for 9 hours at a flow rate of 1.5 L/min, and for 3 hours at a flow rate of 0.75 L/min. Due to equipment difficulties such as pump failures, the injection was not continuous: it was interrupted four times for periods ranging from 10

minutes to an hour. After about five hours of pumping, water was withdrawn from a second source well because the initial source well was not functioning properly.

Water levels in the injection wells were periodically checked to ensure that they did not rise too rapidly. Water levels in the wells rose by about 25 cm, on average. Only one injection well, used for the 85% methanol pulse, was anomalous in that water levels rose by 60 cm and the well briefly overflowed.

A.3 Results of Injection Monitoring

Tables A-1 to A-7 show the results of injection monitoring. Figure A-2 presents plots of concentration vs. time for dissolved oxygen over the course of the injection. In general, solute concentrations were highly variable but comparable for the three pulses.

Table A-1a. Water Level Data for the Injection - July 13, 1988

10% MTBE PULSE

Time	Distance from Top of Well Casing (-100 cm)			Water Level Rise (cm)		
	MTBE1	MTBE2	MTBE3	MTBE1	MTBE2	MTBE3
5:45	194	196	197	0	0	0
7:00	177	186	188	17	10	9
9:00	173	176	173	21	20	24
10:30	173	183	193	21	13	4
12:00	173	177	173	21	19	24
14:00	193	196	199	1	0	-2
15:30	153	157	160	41	39	37
16:30	153	157	133	41	39	64
18:30	148	148	158	46	48	39
Avg.	171	175	175	23	21	22

Table A-1b. Water Level Data for the Injection - July 13, 1988
100% PS-6 PULSE

Time	Distance from Top of Well Casing (-100 cm)			Water Level Rise (cm)		
	PS6-1	PS6-2	PS6-3	PS6-1	PS6-2	PS6-3
5:45	195	200	203	0	0	0
7:00	177	179	179	18	21	24
9:00	173	176	179	22	24	24
10:30	188	196	195	7	4	8
12:00	173	177	179	22	23	24
14:00	193	196	199	2	4	4
15:30	153	157	159	42	43	44
16:30	153	157	130	42	43	73
18:30	153	146	149	42	54	54
Avg.	173	176	175	23	24	28

Table A-1c. Water Level Data for the Injection - July 13, 1988
85% MEOH PULSE

Time	Distance from Top of Well Casing (-100 cm)			Water Level Rise (cm)		
	MEOH1	MEOH2	MEOH3	MEOH1	MEOH2	MEOH3
5:45	196	196	199	0	0	0
7:00	123	167	177	73	29	22
9:00	105	173	173	91	23	26
10:30	113	183	195	83	13	4
12:00	133	163	175	63	33	24
14:00	123	173	185	73	23	14
15:30	149	123	145	47	73	54
16:30	119	193	174	77	3	25
18:30	169	183	195	27	13	4
Avg.	137	173	180	59	23	19

Table A-2a. Injection Solution Concentrations: 100% PS-6 Pulse

Sample Time	Benzene (ug/L)	Toluene (ug/L)	Ethyl-benzene (ug/L)	para-Xylene (ug/L)	meta-Xylene (ug/L)	ortho-Xylene (ug/L)
7:00	5,946	4,005	516	510	1,281	770
7:31	7,514	5,091	652	646	1,607	992
10:15	7,573	4,904	745	732	1,864	1,123
11:35	6,686	3,925	494	480	1,211	790
12:12	9,074	5,289	657	651	1,646	986
12:57	9,910	5,503	691	697	1,721	1,072
14:32	7,684	8,419	2,522	2,614	6,562	3,442
15:40	6,127	4,132	622	636	1,570	924
16:13	12,687	9,691	1,709	1,735	4,389	2,513
16:52	7,012	4,734	690	696	1,726	1,019
17:26	1,670	1,248	202	210	517	286
17:58	7,052	4,524	651	662	1,644	976
18:32	6,662	4,101	580	583	1,439	854
19:19	5,881	4,103	647	652	1,632	957
19:51	6,506	4,596	668	677	1,694	1,008
Average	7,199	4,951	803	812	2,034	1,181
Stand. Dev.	2,274	1,881	550	572	1441	749
Coeff. Var. %	32	38	69	70	71	63
Maximum	12,687	9,691	2,522	2,614	6,562	3,442
Minimum	1,670	1,248	202	210	517	286

Table A-2b. Injection Solution Concentrations: 100% PS-6 Pulse

Sample Time	Chloride (mg/L)	Temp (°C)	pH
7:00	346	16	6.9
7:31	514	17	7.1
10:15	478	23	7.1
11:35	557	21	7.2
12:12	424	18	6.9
12:57	423	20	7.0
14:32	459	19	6.8
15:40	285	18	6.9
16:13	401	18	6.9
16:52	520	18	6.9
17:26	490	16	6.9
17:58	418	17	7.0
18:32	569	18	7.0
19:19	623	18	7.0
19:51	671	16	7.0
Average	479	18	6.9
Stand. Dev.	99	2	0.1
Coeff. of Var. %	21	10	1
Maximum	671	23	7.2
Minimum	285	16	6.8

Table A-3a. Injection Solution Concentrations: 85% Methanol Pulse

Sample Time	Benzene (ug/L)	Toluene (ug/L)	Ethyl-benzene (ug/L)	para-Xylene (ug/L)	meta-Xylene (ug/L)	ortho-Xylene (ug/L)
6:54	7,395	4,626	563	525	1,428	836
8:56	6,595	4,371	530	496	1,341	813
10:20	8,252	5,726	884	830	2,243	1,297
11:40	12,064	6,698	819	746	2,033	1,169
12:17	8,370	4,749	573	549	1,447	870
13:04	7,776	4,401	548	507	1,354	805
14:36	5,883	6,188	1,741	1,807	4,656	2,377
15:44	5,616	4,011	670	682	1,703	979
16:19	13,826	9,518	1,512	1,518	4,036	2,215
16:48	6,164	4,293	697	740	1,639	960
17:32	6,798	5,191	1,086	1,107	2,799	1,545
18:05	7,357	4,450	619	673	1,648	888
18:38	7,028	4,436	619	627	1,566	953
19:28	5,465	3,737	569	558	1,516	796
19:56	7,388	5,051	793	667	1,758	1,026
Average	7,732	5,163	815	802	2,078	1,169
Stand. Dev.	2,238	1,403	353	373	970	485
Coeff. Var. %	29	27	43	46	47	42
Maximum	13,826	9,518	1,741	1,807	4,656	2,377
Minimum	5,465	3,737	530	496	1,341	796

Table A-3b. Injection Solution Concentrations: 85% Methanol Pulse

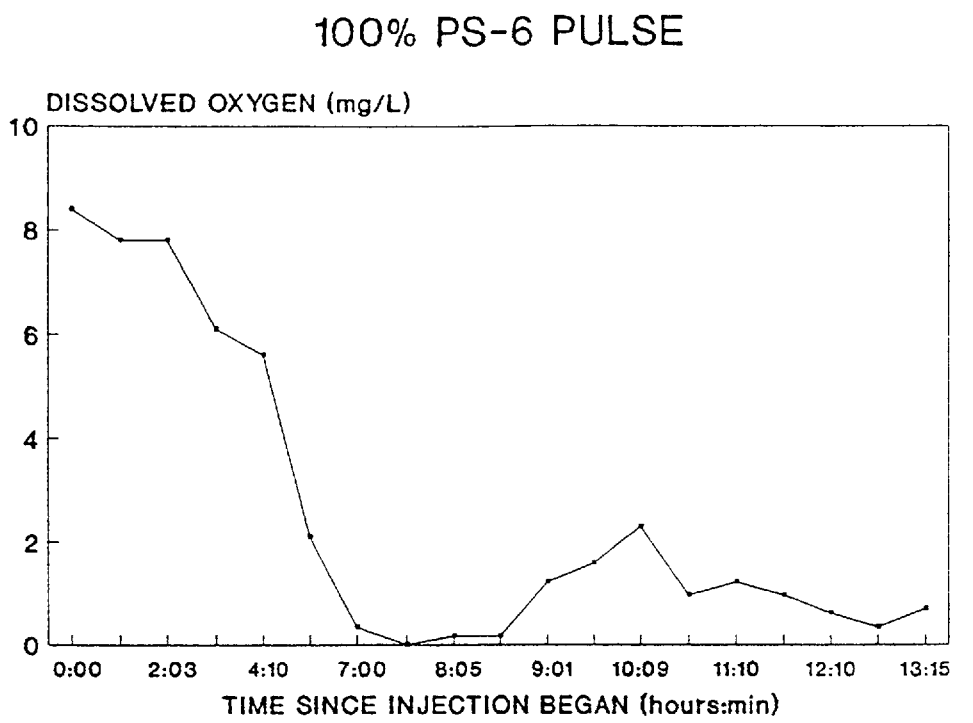
Sample Time	Chloride (mg/L)	Methanol (ug/L)	Temp (°C)	pH
6:54	442	5,929	16	6.5
8:56	554	6,859	21	7.4
10:20	593	7,059	26	7.2
11:40	922	11,493	23	7.3
12:17	647	7,882	22	7.0
13:04	671	7,757	19	7.0
14:36	635	7,447	19	6.9
15:44	635	7,607	19	6.9
16:19	483	6,021	20	6.9
16:48	617	6,723	18	7.0
17:32	587	6,917	18	6.9
18:05	373	6,216	17	7.0
18:38	476	5,729	18	7.0
19:28	520	5,497	17	7.0
19:56	496	6,372	16	7.0
Average	577	7,034	19	7.0
Stand. Dev.	124	1,395	3	0.2
Coeff. of Var. %	21	20	14	3
Maximum	922	11,493	26	7.4
Minimum	373	5,497	16	6.5

Table A-4a. Injection Solution Concentrations: 10% MTBE Pulse

Sample Time	Benzene (ug/L)	Toluene (ug/L)	Ethyl-benzene (ug/L)	para-Xylene (ug/L)	meta-Xylene (ug/L)	ortho-Xylene (ug/L)
6:47	10,394	6,511	810	787	1,980	1,276
7:25	3,931	2,576	339	332	828	496
10:10	7,178	4,500	538	522	1,320	843
10:50	9,966		720	695	1,803	1,104
12:08	8,691	5,492	717	706	1,831	1,099
12:42	6,494	4,097	621	609	1,551	911
14:27	10,106	12,835	4,343	4,504	11,406	5,878
15:34	6,057	4,144	647	644	1,614	952
16:09	12,898	9,293	1,726	1,746	4,391	2,484
16:47	7,194	4,853	777	780	2,401	1,124
17:21	3,263	2,269	369	365	890	517
17:52	9,977	6,364	1,055	1,069	2,679	1,545
18:27	7,412	4,419	611	611	1,518	915
19:14	5,928	3,718	537	532	1,322	777
19:47	5,617	3,818	547	539	1,341	814
Average	7,674	5,349	957	963	2,458	1,382
Stand. Dev.	2,549	2,686	959	1,001	2,533	1,287
Coeff. Var.%	33	50	100	104	103	93
Maximum	12,898	12,835	4,343	4,504	11,406	5,878
Minimum	3,263	2269	339	332	828	496

Table A-4b. Injection Solution Concentrations: 10% MTBE Pulse

Sample Time	Chloride (mg/L)	MTBE (mg/L)	Temp (°C)	pH
6:47	520	320	14	6.1
7:25	390	230	17	7.0
10:10	617	397	23	7.1
10:50	560	336	25	7.3
12:08	529	321	20	7.0
12:42	534	330	19	7.0
14:27	454	320	18	6.9
15:34	563	276	18	6.9
16:09	505	315	19	7.0
16:47	478	307	18	7.0
17:21	460	287	17	7.0
17:52	352	219	17	7.0
18:27	539	160	18	7.0
19:14	623	278	18	7.0
19:47	605	237	16	7.0
Average	515	289	18	6.9
Stand. Dev.	76	56	2	0.2
Coeff. of Var. %	15	19	14	4
Maximum	623	397	25	7.3
Minimum	352	160	14	6.1



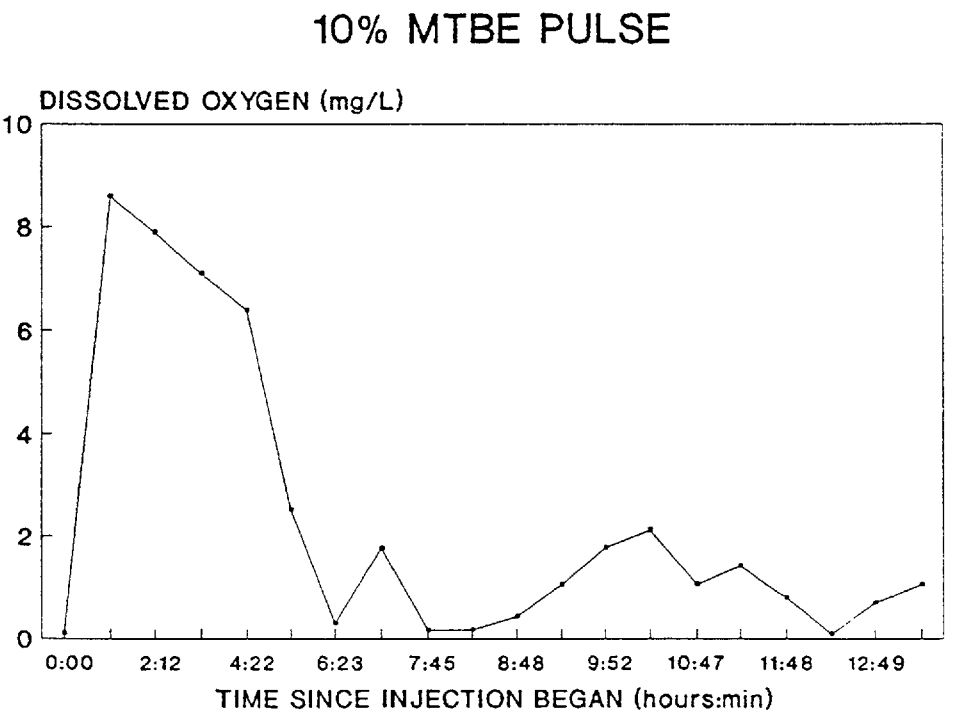


Figure A-2. Plots of Dissolved Oxygen vs. Time for the Injection Solutions.

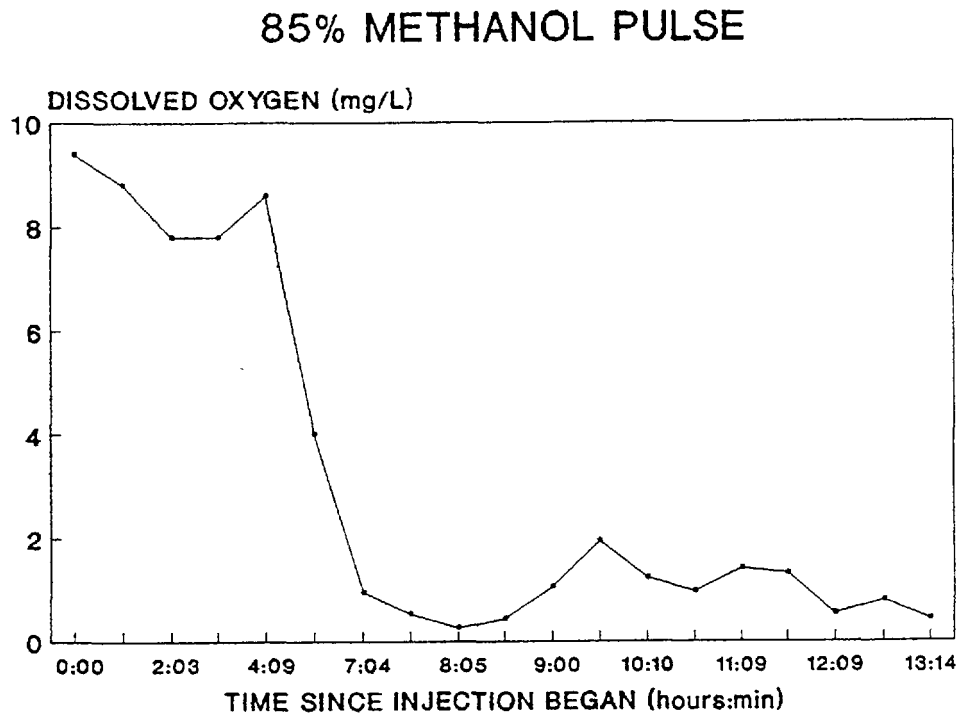


Figure A-2. (continued)

A.4 References

Cherry, J.A., R.W. Gillham, E.G. Anderson, and P.E. Johnson, 1983. Migration of Contaminants at a Landfill: a Case Study. 2. Groundwater Monitoring Devices. Journal Hydrol., Vol. 63, pp 31-49.

Patrick, G.C., 1986. A Natural Gradient Tracer Experiment of Dissolved Benzene, Toluene, and Xylenes in a Shallow Sand Aquifer. Unpublished M.Sc. Thesis, University of Waterloo, Waterloo, Ontario, Canada.

APPENDIX B

THE MONITORING NETWORK

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B.1 Installation of the Monitoring Network

Before the experiment began, the monitoring network consisted of a series of Teflon and polyethylene bundle piezometers installed for previous experiments. Patrick (1986) found that the monoaromatics can penetrate the walls of the polyethylene tubes, and points below the plumes will show a false presence of BTX. For this reason, all polyethylene samplers were replaced with Teflon devices prior to injection. Patrick also showed that the Teflon tubing used to construct the piezometers will sorb and desorb significant quantities of BTEX. However, at the piezometer densities and contact times of this experiment, solute behavior was not expected to be significantly affected by the use of Teflon samplers.

A schematic diagram of a typical piezometer from this study is shown in Figure B-1. 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 tube ends at ground surface are numbered, and they vary in length so that points can be easily distinguished if the labels are lost. The first point has the longest tube and the last has the shortest, with graded lengths between.

To improve the density of the existing monitoring network in the vicinity of each solute pulse, 75 additional samplers were installed during the week of June 20, 1988 using the jetting of casing method. They each had 14 sample points spaced at 0.2 m intervals, and spanned a depth of 1.8 m to 4.4 m below ground surface.

After the plumes had been sampled three times, a further extension of the network was necessary. A preliminary analysis of the trajectories of the solute centers of mass was made, and an extension of the grid network was designed by Lloyd Lemon of the Waterloo Center for Groundwater Research. The new portion of the network differed from those used for previous tracer tests in that the piezometers were offset to improve the

resolution in the direction transverse to groundwater flow. All were constructed with a sample point spacing of 0.2 cm because little vertical dispersion was expected. Piezometer density decreased with distance from the source because the plumes were expected to spread substantially in the longitudinal direction. The sample points spanned a deeper interval further from the source because plumes gradually sank in previous experiments at the site (Mackay *et al.*, 1986).

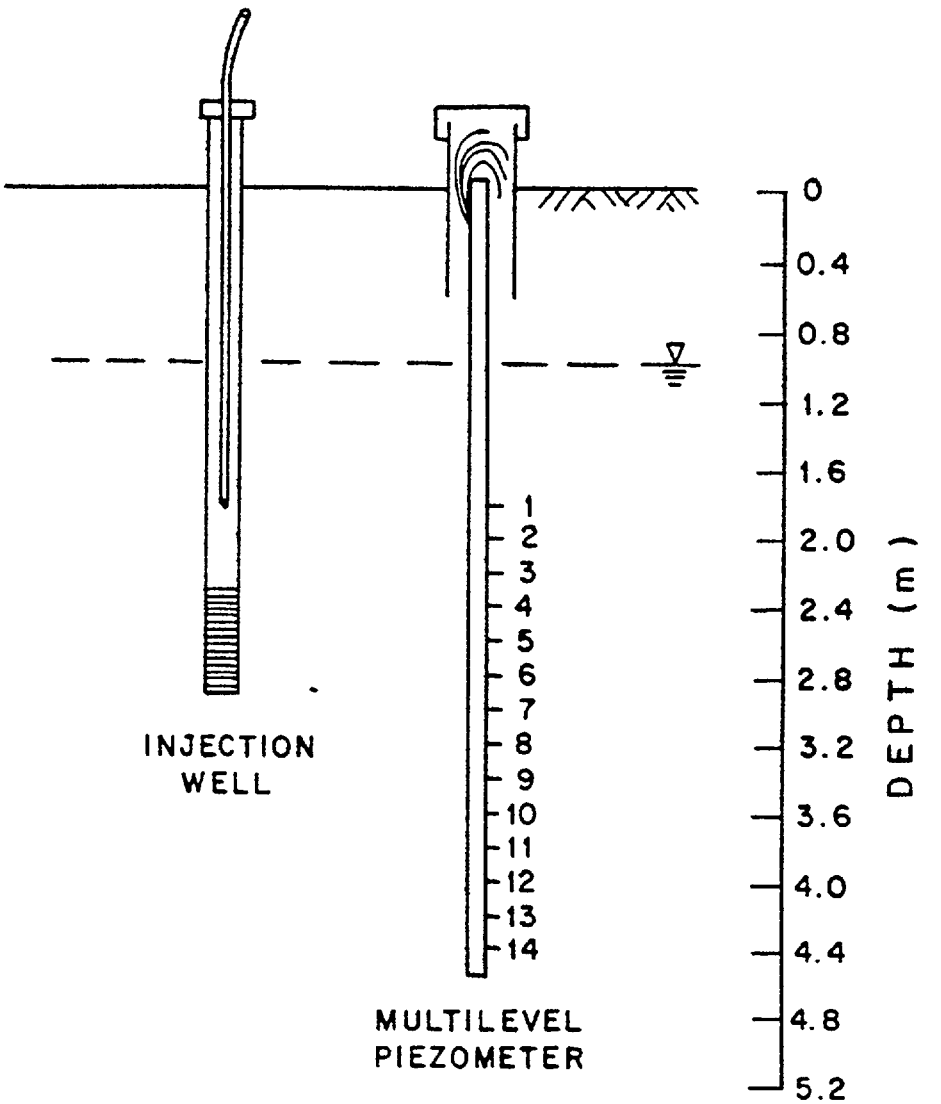

Figure B-1. Schematic diagram of a multilevel sampler and an injection well (after Patrick 1986).

A total of 150 piezometers were installed during the week of May 8, 1989. Any screens that were disturbed during transport were replaced. At the time of the installation of these piezometers, most of the solutes had migrated beyond the existing grid, so many of the new piezometers were installed directly into the solute clouds. A drive method of installation, which requires no addition of water to the formation, was used in order to cause minimal disturbance to the plumes.

The piezometers were installed by first driving a two inch hollow iron drill rod loosely fitted with a PVC drive point to the desired depth, using a drill rig. The Teflon bundles were dropped down the center of the drill rod, and the rod was removed, leaving the drive point and the piezometer in place. In the saturated zone, the sand immediately collapsed around the bundle. A plastic casing was then driven about half a meter into the ground over the top of the piezometer and capped to protect the tubes. The method does involve minor aquifer disturbance: researchers have excavated similar piezometer installations and found that the sand layers tend to bend downward by about ten centimeters around the piezometer stalk (R. Starr, 1991 pers. comm.).

The newly installed piezometers were developed by attaching tubing to each of the fourteen points and pumping simultaneously into a container. A total of one liter of groundwater was removed from each piezometer during development. Based on the number of piezometers intersecting the plumes and the average concentrations of the solutes, less than 1% of the mass of the plumes is estimated to have been removed during piezometer development.

B.2 Piezometer Positions and Specifications

Table B-1 lists the specifications for all of the sampling devices present in the final monitoring array. Accurate records from earlier experiments were not consistently available, so some of the information is inferred. All of the x-y coordinates for the piezometers are known with certainty. The depth of the first point and the spacing of the

sample points have been inferred for the Stanford samplers by examining the spatial coordinates of concentration values in the Stanford-Waterloo database. More reliable data can probably be obtained from Stanford University.

Table B-1. Positions and Specifications for the Multilevel Samplers

PIEZO NO.	X	Y	DATE INSTALLED	INSTALLED BY	METHOD	NUMBER OF POINTS	DEPTH OF FIRST POINT (m)	VERTICAL SPACING (m)	DEPTH OF BOTTOM POINT (m)	COMMENTS
I.W.	-4	-1	??-JUN-88	LEMON	WASH	SCREEN	2.3	0.6	2.9	MTBE
I.W.	-4	0	??-JUN-88	LEMON	WASH	SCREEN	2.3	0.6	2.9	MTBE
I.W.	-4	1	??-JUN-88	LEMON	WASH	SCREEN	2.3	0.6	2.9	MTBE
I.W.	0	-1	??-JUN-88	LEMON	WASH	SCREEN	2.3	0.6	2.9	PS-6
I.W.	0	0	??-JUN-88	LEMON	WASH	SCREEN	2.3	0.6	2.9	PS-6
I.W.	0	1	??-JUN-88	LEMON	WASH	SCREEN	2.3	0.6	2.9	PS-6
I.W.	4	-1	??-JUN-88	LEMON	WASH	SCREEN	2.3	0.6	2.9	METHANOL
I.W.	4	0	??-JUN-88	LEMON	WASH	SCREEN	2.3	0.6	2.9	METHANOL
I.W.	4	1	??-JUN-88	LEMON	WASH	SCREEN	2.3	0.6	2.9	METHANOL
N3-N4	-5	-1.5	24-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N3-N3	-4	-1.5	24-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N3-N2	-3	-1.5	24-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N3-N1	-1	-1.5	22-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N3-0	0	-1.5	23-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N3-1	1	-1.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N3-2	3	-1.5	20-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N3-3	4	-1.5	20-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N3-4	5	-1.5	20-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N2-N3	-4.5	-1	24-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N2-N2	-3.5	-1	24-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N2-N1	-0.5	-1	23-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N2-1	0.5	-1	22-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N2-2	3.5	-1	20-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N2-3	4.5	-1	20-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N1-N5	-5	-0.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N1-N4	-4	-0.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N1-N3	-3	-0.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N1-N2	-2	-0.5	24-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N1-N1	-1	-0.5	23-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N1-0	0	-0.5	23-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N1-1	1	-0.5	22-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N1-2	2	-0.5	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
N1-3	3.5	-0.5	??-APR-86	BERRY-SPARK	WASH	14	1.8	0.2	4.4	RENUMBERED
N1-4	4	-0.5	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
N1-5	5.2	-0.5	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
O-N3	-4.5	0	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
O-N2	-3.5	0	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
O-N1	-0.5	0	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
O-1	0.5	0	23-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
C2	3	0	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
O-2	3.5	0	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
O-3	4.5	0	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OA-N5	-5	0.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	RMVD 18-OCT-88
OA-N4	-4	0.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OA-N3	-3	0.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OA-N2	-2	0.5	23-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OA-N1	-1	0.5	23-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OA-0	0	0.5	22-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OA-1	1	0.5	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OA-2	2	0.5	22-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
C5	3	0.5	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
C4	4	0.5	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
OA-5	5	0.5	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OB-N3	-4.5	1	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OB-N2	-3.5	1	01-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OB-N1	-0.5	1	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
C10	0.5	1	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
OB-2	3.5	1	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
OB-3	4.5	1	01-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
1-N5	-5	1.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	

Table B-1. Continued

PIEZO NO.	X	Y	DATE INSTALLED	INSTALLED BY	METHOD	NUMBER OF POINTS	DEPTH OF FIRST POINT (m)	VERTICAL SPACING (m)	DEPTH OF BOTTOM POINT (m)	COMMENTS
1-N4	-4	1.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
1-N3	-3	1.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
1-N2	-2	1.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
1-N1	-1	1.5	??-JUL-84	PATRICK	WASH	12	1.7	0.2	3.9	
1-0	0	1.5	??-JUL-84	PATRICK	WASH	12	1.7	0.2	3.9	
1-1	1	1.5	??-APR-86	BERRY-SPAR	WASH	12	1.7	0.2	3.9	
1-2	2	1.5	??-APR-86	BERRY-SPAR	WASH	12	1.7	0.2	3.9	
1-3	3	1.5	??-APR-86	BERRY-SPAR	WASH	12	1.7	0.2	3.9	
1-4	4	1.5	??-APR-86	BERRY-SPAR	WASH	12	1.7	0.2	3.9	
1-5	5	1.5	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
1A-N2	-4.5	2	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
1A-N1	-3.5	2	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
C16	-3	2	??-APR-86	BERRY-SPAR	WASH	14	1.7	0.2	4.3	
C15	0.5	2	??-APR-86	BERRY-SPAR	WASH	14	1.7	0.2	4.3	
C14	1	2	??-APR-86	BERRY-SPAR	WASH	14	1.7	0.2	4.3	
1A-2	3.5	2	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
1A-3	4.5	2	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
2-N4	-5	2.5	27-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
2-N3	-3.75	2.5		STANFORD		14	2.0	0.2	4.6	
2-N2	-2.5	2.5		STANFORD		14	2.0	0.2	4.6	
2-N1	-1.25	2.5		STANFORD		14	2.0	0.2	4.6	
2-0	0	2.5	21-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
2-1	1.25	2.5		STANFORD		14	2.0	0.2	4.6	
2-2	2.5	2.5	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
2-3	3.75	2.5	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
2-4	5	2.5	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
3-N4	-5	3.5	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
3-N3	-3.75	3.5		STANFORD		14	2.0	0.2	4.6	
3-N2	-2.5	3.5		STANFORD		14	2.0	0.2	4.6	
3-N1	-1.25	3.5		STANFORD		14	2.0	0.2	4.6	
3-0	0	3.5	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
3-1	1.25	3.5		STANFORD		14	2.1	0.2	4.7	
3-2	2.5	3.5		STANFORD		14	2.1	0.2	4.7	
3-3	3.75	3.5		STANFORD		14	2.1	0.2	4.7	
3-4	5	3.5		STANFORD		14	2.0	0.2	4.6	
3A-N3	-4.41	4.34	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
3A-N2	-3.14	4.34	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
3A-N1	-1.95	4.27	28-JUN-88	LEMON	WASH	14	1.8	0.2	4.4	
C20	0.5	4.25	??-APR-86	BERRY-SPAR	WASH	14	1.7	0.2	4.3	
C19	3.25	4.25	??-APR-86	BERRY-SPAR	WASH	14	1.7	0.2	4.3	
4-N4	-5	5		STANFORD		14	2.1	0.2	4.7	
4-N3	-3.75	5		STANFORD		14	2.1	0.2	4.7	
4-N2	-2.5	5		STANFORD		14	2.1	0.2	4.7	
4-N1	-1.25	5		STANFORD		14	2.0	0.2	4.6	
4-0	0	5		STANFORD		14	2.1	0.2	4.7	
4-1	1.25	5		STANFORD		14	2.0	0.2	4.6	
4-2	2.5	5		STANFORD		14	2.0	0.2	4.6	
4-3	3.75	5		STANFORD		14	2.1	0.2	4.7	
4-4	5	5		STANFORD		14	2.0	0.2	4.6	
4A-N2	-4.5	5.5	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
4A-N1	-2	5.5	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
4A-0	0	5.5	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
C22	2	5.5	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
C21	4.5	5.5	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
5-N3	-3.75	6.5		STANFORD		14	2.0	0.2	4.6	
5-N2	-2.5	6.5		STANFORD		14	2.0	0.2	4.6	
5-N1	-1.25	6.5		STANFORD		14	2.1	0.2	4.7	
5-0	0	6.5		STANFORD		14	2.1	0.2	4.7	
5-1	1.25	6.5		STANFORD		14	2.1	0.2	4.7	
5-2	2.5	6.5		STANFORD		14	2.1	0.2	4.7	
5-3	3.75	6.5		STANFORD		14	2.1	0.2	4.7	

Table B-1. Continued

PIEZO NO.	X	Y	DATE INSTALLED	INSTALLED BY	METHOD	NUMBER OF POINTS	DEPTH OF FIRST POINT (m)	VERTICAL SPACING (m)	DEPTH OF BOTTOM POINT (m)	COMMENTS
5-4	5	6.5		STANFORD		14	2.1	0.2	4.7	
5-5	6.25	6.5		STANFORD		20	1.7	0.2	5.5	
6-N3	-4.5	8		STANFORD		14	2.0	0.2		
6-N2	-3	8		STANFORD		14	2.0	0.2		
6-N1	-1.5	8		STANFORD		14	2.1	0.2	4.7	
6-0	0	8		STANFORD		14	2.0	0.2	4.6	
6-1	1.5	8		STANFORD		14	2.0	0.2	4.6	
6-2	3	8		STANFORD		14	2.1	0.2	4.7	
6-3	4.45	8		STANFORD		14	2.0	0.2	4.6	
6-4	5.9	8		STANFORD		14	2.0	0.2	4.6	
6-5	7.4	8		STANFORD		14	1.8	0.2	4.4	
6A-N2	-3	9	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
6A-N1	-1	9	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
6A-1	1	9	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
C25	2.25	9		BERRY-SPARK	WASH	14	1.7	0.2	4.3	
6A-3	2.85	9	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
6A-4	4	9	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
6A-5	5	9	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
6A-6	6	9	12-JUL-88	LEMON	PUSH	14	1.8	0.2	4.4	
6A-7	7	9	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
7-N3	-4.5	10		STANFORD		20	1.1	0.2	4.9	EXT CNTR STALK
7-N2	-3	10		STANFORD		20	1.1	0.2	4.9	EXT CNTR STALK
7-N1	-1.5	10		STANFORD		20	1.1	0.2	4.9	EXT CNTR STALK
7-0	0	10		STANFORD		20	1.1	0.2	4.9	EXT CNTR STALK
7-1	1.5	10		STANFORD		20	1.1	0.2	4.9	EXT CNTR STALK
7-2	3	10		STANFORD		20	1.1	0.2	4.9	EXT CNTR STALK
7-3	4.6	10		STANFORD		20	1.1	0.2	4.9	EXT CNTR STALK
7-4	6	10		STANFORD		20	1.1	0.2	4.9	EXT CNTR STALK
7-5	7.5	10		STANFORD		20	1.1	0.2	4.9	EXT CNTR STALK
7A-N3	-3.75	11	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
7A-N2	-2.25	11	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
7A-N1	-0.75	11	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
7A-1	0.75	11	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
7A-2	2.25	11	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
7A-3	3.75	11	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
7A-4	5.25	11	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
7A-5	6.75	11	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
7B-N3	-4.5	12	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
7B-N2	-3	12	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
7B-N1	-1.5	12	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
7B-0	0	12	??-APR-86	PATRICK	WASH	14	1.7	0.3	5.6	
7B-1	2	12	??-APR-86	PATRICK	WASH	14	1.7	0.3	5.6	
7B-2	3.5	12	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
7B-3	5	12		STANFORD		12	1.7	0.2	3.9	
7B-4	6.5	12		STANFORD		12	1.7	0.2	3.9	
7B-5	8	12		STANFORD		12	1.7	0.2	3.9	
8-N2	-4	13	??-APR-86	PATRICK	WASH	14	1.4	0.3	5.3	
8-N1	-2	13	??-APR-86	PATRICK	WASH	14	1.4	0.3	5.3	
8-0	0	13	??-APR-86	PATRICK	WASH	14	1.4	0.3	5.3	
8-1	2	13	??-APR-86	PATRICK	WASH	14	1.4	0.3	5.3	
8-2	4	13	??-APR-86	PATRICK	WASH	27	1.4	0.2	6.6	
8-3	6	13	??-APR-86	PATRICK	WASH	14	1.4	0.3	5.3	
8-4	8	13	??-APR-86	PATRICK	WASH	14	1.4	0.3	5.3	
8-5	10	13	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
8-6	12	13	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
8A-N2	-3	13.5	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
8A-N1	-1	13.5	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
8A-1	1	13.5	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
8A-2	3	13.5	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
8A-3	5	13.5	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	
8A-4	7	13.5	18-OCT-88	LEMON	PUSH	14	1.8	0.2	4.4	

Table B-1. Continued

PIEZO NO.	X	Y	DATE INSTALLED	INSTALLED BY	METHOD	NUMBER OF POINTS	DEPTH OF FIRST POINT (m)	VERTICAL SPACING (m)	DEPTH OF BOTTOM POINT (m)	COMMENTS
8B-N2	-4	14.25	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
8B-N1	-2	14.25	??-APR-86	BERRY-SPARK	WASH	12	1.7	0.2	3.9	
8B-0	0	14.25	??-APR-86	BERRY-SPARK	WASH	12	1.7	0.2	3.9	
8B-1	2	14.25	??-APR-86	BERRY-SPARK	WASH	12	1.7	0.2	3.9	
8B-2	4	14.25	??-APR-86	BERRY-SPARK	WASH	12	1.7	0.2	3.9	
8B-3	6	14.25	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
8B-4	8	14.25	??-APR-86	BERRY-SPARK	WASH	14	1.7	0.2	4.3	
9-N1	-3	15.5	??-APR-86	PATRICK	WASH	14	1.8	0.3	5.7	
9-0	0	15.5	??-APR-86	PATRICK	WASH	14	1.8	0.3	5.7	
9-1	3	15.5	??-APR-86	PATRICK	WASH	14	1.8	0.3	5.7	
9-2	6	15.5	??-APR-86	PATRICK	WASH	14	1.8	0.3	5.7	
9-3	9	15.5	??-APR-86	PATRICK	WASH	14	1.8	0.3	5.7	
9-4	12	15.5	??-APR-86	PATRICK	WASH	14	1.8	0.3	5.7	
9B-N2	-3	16.75	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
9B-N1	-1	16.75	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
9B-1	1.5	16.75	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
9B-2	4.5	16.75	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
9B-3	7.5	16.75	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
9B-4	10.5	16.75	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
10-N2	-4	18	11-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
10-N1	-2	18	11-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
10-0	0	18		PATRICK	WASH	14	1.8	0.3	5.7	
10-1	1.5	18		PATRICK	WASH	14	1.8	0.3	5.7	
10-2	3	18		PATRICK	WASH	14	1.8	0.3	5.7	
10-3	4.5	18	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	REPLACEMENT
10-4	6	18		PATRICK	WASH	25	1.8	0.2	6.6	
10-5	7.5	18		STANFORD		23	1.7	0.2	6.1	
10-6	9	18		STANFORD		14	1.7	0.3	5.6	
10-7	12	18		STANFORD		14	2.4	0.3	6.3	
10-8	15	18		STANFORD		14	2.4	0.2	5.0	
11-N2	-3	19.5	11-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
11-N1	-1.5	19.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
11-0	0	19.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
11-1	1.5	19.5		STANFORD		14	1.8	0.3	5.7	
11-2	3	19.5		STANFORD		14	1.8	0.3	5.7	
11-3	4.5	19.5		STANFORD		14	1.8	0.3	5.7	
11-4	6	19.5		STANFORD		14	1.8	0.3	5.7	
11-5	7.5	19.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	REPLACEMENT
11-6	9	19.5		STANFORD		14	1.8	0.3	5.7	
11-7	10.5	19.5		STANFORD		14	1.8	0.2	4.4	
11-8	12	19.5		STANFORD		20	1.8	0.2	5.6	
11-9	15	19.5		STANFORD		14	1.8	0.2	4.4	
11B-10	13.5	20.2		STANFORD		14	1.8	0.2	4.4	
12-N1	-3	21	11-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
12-0	0	21		STANFORD		14	1.8	0.3	5.7	
12-1	3	21		STANFORD		14	1.8	0.3	5.7	
12-2	6	21		STANFORD		14	1.7	0.3	5.6	
12-3	9	21		STANFORD		14	1.8	0.3	5.7	
12-4	12	21		STANFORD		14	1.8	0.3	5.7	
12-5	15	21		STANFORD		14	2.3	0.3	6.2	
13-N2	-4.5	22.5	11-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
13-N1	-1.5	22.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
13-1	1.5	22.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
13-2	4.5	22.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
13-3	7.5	22.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
13-4	10.5	22.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
13-5	13.5	22.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
14-N1	-3	24	11-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
14-0	0	24	11-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
14-1	3	24		STANFORD		14	1.7	0.3	5.6	
14-2	6	24		STANFORD		14	1.8	0.3	5.7	

Table B-1. Continued

PIEZO NO.	X	Y	DATE INSTALLED	INSTALLED BY	METHOD	NUMBER OF POINTS	DEPTH OF FIRST POINT (m)	VERTICAL SPACING (m)	DEPTH OF BOTTOM POINT (m)	COMMENTS
14-3	9	24		STANFORD		14	1.8	0.3	5.7	
14-4	12	24		STANFORD		14	1.7	0.3	5.6	
14-5	15	24		STANFORD		14	1.8	0.3	5.7	
15-N1	-1.5	25.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
15-1	1.5	25.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
15-2	4.5	25.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
15-3	7.5	25.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
15-4	10.5	25.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
15-5	13.5	25.5	08-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
16-N1	-3	27	12-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
16-0	0	27	12-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
16-1	3	27	12-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
16-2	6	27		STANFORD		14	2.4	0.3	6.3	
16-3	9	27		STANFORD		14	2.3	0.3	6.2	
16-4	12	27		STANFORD		14	2.3	0.3	6.2	
16-5	15	27		STANFORD		14	2.4	0.3	6.3	
16-6	18.25	27		STANFORD		16	2.4	0.2	5.4	
17-N1	-1.5	29	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
17-1	1.5	29	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
17-2	4.5	29	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
17-3	7.5	29	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
17-4	10.5	29	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
17-5	13.5	29	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
18-0	0	31	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
18-1	3	31	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
18-2	6	31	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
18-3	9	31		STANFORD		14	2.3	0.3	6.2	
18-4	12	31		STANFORD		14	2.4	0.3	6.3	
18-5	15	31		STANFORD		14	2.3	0.3	6.2	
19-N1	-2	33	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
19-1	2	33	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
19-2	6	33	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
19-3	10	33	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
19-4	14	33	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
20-0	0	35	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
20-1	4	35	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
20-2	8	35	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
20-3	10	35.2		STANFORD		14	2.0	0.3	5.9	
20-4	12	35	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
20-5	15	35		STANFORD		14	2.4	0.3	6.3	
20-6	17.5	35	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
21-N1	-2	37	12-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
21-1	2	37	12-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
21-2	6	37	12-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
21-3	10	37	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
21-4	14	37	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
22-0	0	39	12-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
22-1	4	39	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
22-2	8	39	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
22-3	12	39	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
22-4	16	39	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
23-1	2	41	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
23-2	6	41	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
23-3	10	41	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
23-4	14	41	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
23-5	18	41	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
24-0	0	44		STANFORD		14	1.9	0.3	5.8	
24-1	4	43.8		STANFORD		14	1.9	0.3	5.8	
24-2	8	44.5		STANFORD		14	1.9	0.3	5.8	
24-3	12	44.2		STANFORD		14	1.9	0.3	5.8	
24-4	16	44	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	

Table B-1. Continued

PIEZO NO.	X	Y	DATE INSTALLED	INSTALLED BY	METHOD	NUMBER OF POINTS	DEPTH OF FIRST POINT (m)	VERTICAL SPACING (m)	DEPTH OF BOTTOM POINT (m)	COMMENTS
25-1	2	45	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
25-2	6	45	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
25-3	10	45	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
25-4	14	45	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
25-5	18	45	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
26-0	0	47	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
26-1	4	47	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
26-2	8	47	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
26-3	12	47	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
26-4	16	47	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
26-5	20	47	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
27-1	2	49	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
27-2	6	49	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
27-3	10	49	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
27-4	14	49	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
27-5	18	49	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
28-1	4	51	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
28-2	8	51	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
28-3	12	51	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
28-4	16	51	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
28-5	20	51	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
28B-2	9.55	52		STANFORD		14	1.9	0.3	5.8	
28B-1	5.55	52.5		STANFORD		14	1.9	0.3	5.8	
29-1	2	53	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
29-4	14	53	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
29-5	18	53	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
30-1	4	55	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
30-2	8	55	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
30-3	12	55	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
30-4	16	55	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
30-5	20	55	09-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
31-1	2	57	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
31-2	6	57	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
31-3	10	57	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
31-4	14	57	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
31-5	18	57	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
32-1	4	59	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
32-2	8	59	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
32-3	12	59	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
32-4	16	59	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	
32-5	20	59	10-MAY-89	LEMON	PUSH	14	1.8	0.2	4.4	

B.3 References

Mackay, D., D.L. Freyberg, P.V. Roberts, and J.A. Cherry, 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer. 1. Approach and Overview of Plume Movement. Water Resources Research, Vol. 22, No. 13, pp. 2017-2029.

Patrick, G.C., 1986. A Natural Gradient Tracer Experiment of Dissolved Benzene, Toluene, and Xylenes in a Shallow Sand Aquifer. Unpublished M.Sc. Thesis, University of Waterloo, Waterloo, Ontario, Canada.

APPENDIX C

SAMPLE COLLECTION PROCEDURES AND QUALITY CONTROL

Contents:

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C.1 Prescreening Technique

Over 200 days passed between the third and fourth sampling rounds, so the exact location of the plumes was not certain for the fourth sample event. For this round, a portable TIP photovac air analyzer was used as a prescreening device to delineate the general locale of the plumes. About 250 mL of water was removed from points 3, 5, and 7 of selected piezometers into 500 mL glass jars and sealed. The end of the TIP photovac (calibrated to benzene) was placed in the sample headspace and its value recorded. The plumes were broadly delineated, and the survey results compared well with the organics data obtained from water analyses for the fourth sample round.

C.2 Sample Collection Procedures

Samples for organics and chloride were taken using two sampling carts equipped with peristaltic pumps. Each cart was capable of sampling fourteen tubes of a given multilevel piezometer simultaneously. A schematic diagram of one loop of this sampling device is shown in Figure C-1.

Groundwater samples were collected directly into 18 mL glass hypovials for organics analysis, and into 20 mL polyethylene bottles for chloride analysis. 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.

The groundwater contacted only Teflon, stainless steel, and glass prior to filling of the organics vial. Each well took 20 minutes to half an hour to sample, and the organics can be considered essentially nonsorbing for those surfaces in this timeframe.

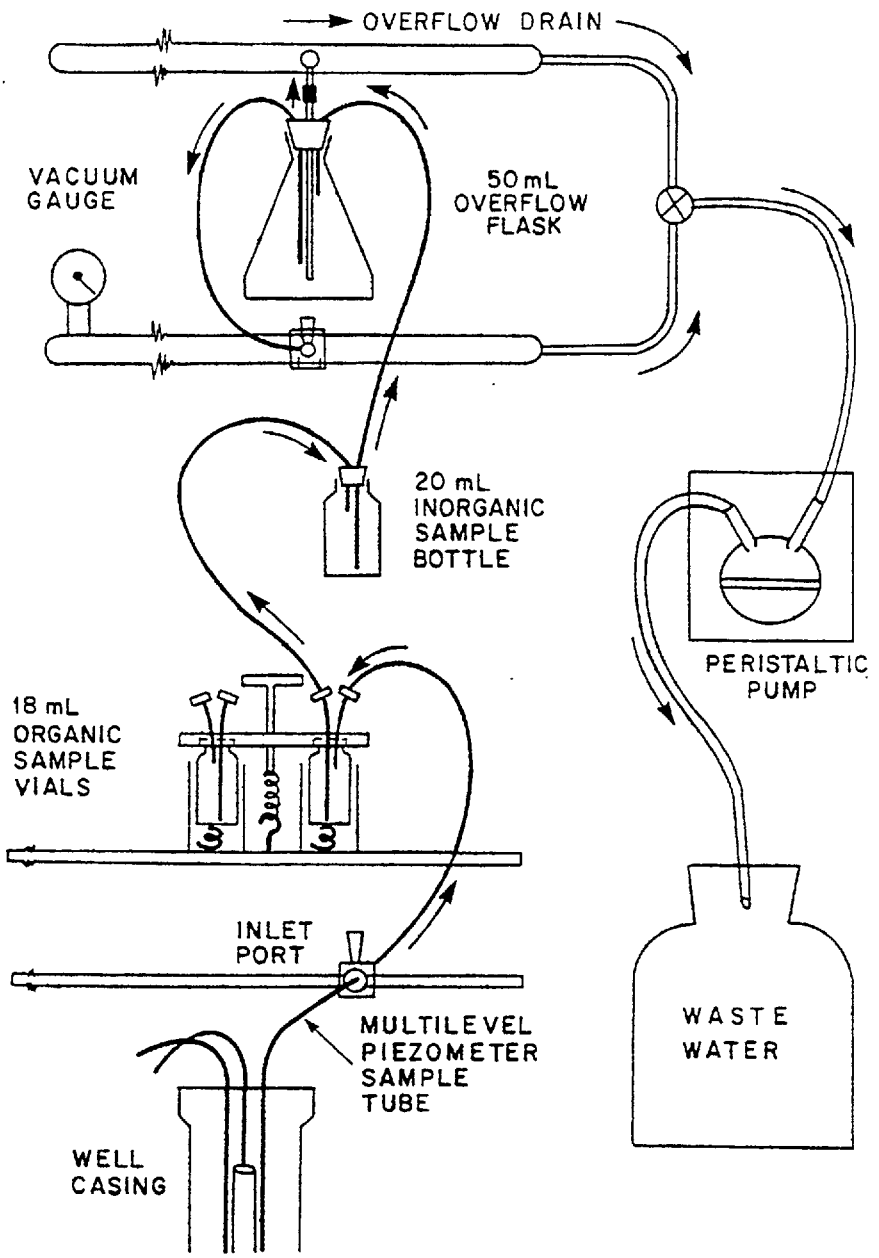

Figure C-1. Schematic diagram of the sample collection system. The device has the capacity to sample fourteen points simultaneously: the sample loop for only one is shown here.

To prevent biotransformation of the solutes after sample collection, 0.1 mL of a 10% sodium azide solution (v/v) was added to each hypovial with a syringe prior to capping. In a previous test at the site, Patrick (1986) saw mass losses in unamended sample vials within 4-6 days of collection. Sodium azide has been shown to be an effective sterilent for time periods on the order of months (Berry-Spark *et al.*, 1987), and samples were analyzed within two weeks for this experiment. The samples received no exposure to the atmosphere except for a few seconds while the sodium azide was added, and the vials were capped with Teflon-lined silicon septa.

Patrick (1986) found that the septa used for capping the hypovials could represent a source of contamination by the monoaromatics. Hypovials and septa were therefore cleaned thoroughly before transport to the field. The hypovials were soaked in commercial alkaline cleaning solution, rinsed with deionized water, dilute nitric acid, and more deionized water. The septa were prepared by boiling in water for one hour. The hypovials and septa were baked overnight at 110°C, then wrapped in foil for transport.

Dissolved oxygen samples were collected by attaching a 50 mL glass syringe to a peristaltic pump and running the pump at the lowest rate. The syringes were flushed once, and then filled. The sample collection procedure permitted no opportunity for exposure of the sample to atmospheric oxygen. Dissolved oxygen analyses were performed onsite with continual re-use of about 20 syringes. The syringes were thoroughly rinsed with deionized water between samples.

C.3 Equipment Blanks

To test the possibility of cross contamination by the manifold, one set of equipment blanks was taken during the fifth sample round of this study. A piezometer situated in the center of the solute clouds, which was known to have high concentrations of the monoaromatics, was sampled. The manifold was then used to sample organic-free water from a Teflon bag. Results of the equipment blanks are presented in Table C-1. Only

one solute, benzene, was detected in one point. The monoaromatics were not detectable in the remaining samples.

Table C-1. Results from Day 398 Equipment Blanks (ug/L)

Manifold Port	Benzene	Toluene	Ethyl-Benzene	para-Xylene	meta-Xylene	ortho-Xylene
1	11.06	0.00	4.48*	0.00	0.00	0.00
2	0.00	0.00	0.00	0.00	0.00	0.00
3	0.00	0.00	3.45*	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.00	0.00	0.00	0.00	0.00
6	0.00	0.00	0.00	0.00	0.00	0.00
7	0.00	0.00	0.00	0.00	0.00	0.00
8	0.00	0.00	0.00	0.00	0.00	0.00
9	0.00	0.00	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00	0.00
14	0.00	0.00	0.00	0.00	0.00	0.00

* found in laboratory blanks

C.4 References

Patrick, G.C., 1986. A Natural Gradient Tracer Experiment of Dissolved Benzene, Toluene, and Xylenes in a Shallow Sand Aquifer. Unpublished M.Sc. Thesis, Earth Sciences Department, University of Waterloo, Waterloo, Ontario, Canada.

Berry-Spark, K.L., J.F. Barker, K.T. MacQuarrie, D. Major, C.I. Mayfield, and E.A. Sudicky, 1988. *The Behavior of Soluble Petroleum Product-Derived Hydrocarbons in Groundwater*. Petroleum Association for the Conservation of the Canadian Environment. PACE Phase III Report No. 85-3.

APPENDIX D

LABORATORY ANALYTICAL PROCEDURES AND QUALITY CONTROL DATA

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D.1 Monoaromatics

The monoaromatics were analyzed by solvent extraction followed by gas chromatography. The technique is more rapid than conventional purge and trap methods, but carries a similar level of accuracy. It was developed specifically for a previous natural gradient tracer test, in which a large number of sample analyses were required in a short time period. The method is described in detail by Patrick *et al.* (1986).

Samples were first brought to room temperature, and then solvent extracted. A vent needle was inserted through the septum of the sample vial, and 1 mL of water was removed. This water was placed in a 1.5 mL glass vial, which was sealed with a Teflon-faced septum and screw cap and refrigerated for subsequent oxygenate analysis. A 0.5 mL aliquot of hexane containing the internal standard m-fluorotoluene was then added to the sample vial and the vent syringe was removed. The vial was placed on its side on a platform shaker and agitated for at least ten minutes. It was then inverted and the water and hexane phases separated.

Sample vials were then set upright and a vent syringe was inserted into the septum. Approximately 3 uL of the hexane was removed from the vial and injected into a Shimadzu gas chromatograph equipped with a split injection port, capillary column, a flame ionization detector and an electronic integrator. Operating conditions for the instrument are shown in Table D-1. Sample run times were about 4-5 minutes.

Table D-1. Analytical Information for the Monoaromatics.

Operating Conditions

Injection Port Temp.	200 °C
Oven Temp.	90 °C
Detector Temp.	300 °C
Column flow rate	5 mL/min.

Method Detection Limits

Compound	N	X (ug/L)	Xo (ug/L)	S%	E%	MDL
Benzene	7	4.3+/-0.7	3.7	13	+16	1.8
Toluene	7	3.2+/-.05	3.6	13	-11	1.4
p-Xylene	7	3.1+/-0.2	3.6	5.8	-14	0.6
m-Xylene	7	4.4+/-0.3	3.7	5.7	+19	0.8
o-Xylene	7	3.8+/-0.4	3.7	9.7	+3	1.2

Accuracy and Precision at Typical Sample Concentrations

Compound	N	(ug/L)	Xo (ug/L)	S%	E%
Benzene	31	84.5+/-1.9	85.2	4.2	-1
Toluene	31	83.8+/-0.9	83.7	2.9	0
p-Xylene	31	83.3+/-1.5	83.5	2.4	0
m-Xylene	31	86.2+/-1.5	85.6	2.8	+1
o-Xylene	31	86.6+/-1.6	85.7	2.0	+1

Analysis of USEPA Quality Control Sample WP 879 #1

Compound	N	X (ug/L)	Xo (ug/L)	S%	E%
Benzene	7	30.6+/-1.1	30.7	3.0	0
Toluene	7	5.6+/-0.4	4.1	6.1	+37
p-Xylene	7	20.5+/-0.4	19.1	1.8	+7
m-Xylene	7	45.3+/-0.9	42.6	1.7	+6
o-Xylene	7	12.1+/-0.4	10.6	2.5	+14

KEY to Table D-1: N : number of replicate determinations
X : mean of replicate determinations, 99% confidence level
Xo : true value
S% : relative standard deviation
E% : average relative error
MDL: method detection limit

The gas chromatograph was calibrated at the start of each sample analysis day by averaging the runs for three standard replicates. A stock standard containing about 3,000 ug/L of each compound was used for the initial calibration. A less concentrated standard, which contained about 300 ug/L of each compound, was run routinely after every tenth sample as a check on the instrument calibration, and adjustments were made when necessary.

The stock standards were prepared gravimetrically by injecting the pure-phase compounds into a 60 mL aliquot of methanol and diluting volumetrically with one liter of reagent water. They were then mixed with a magnetic stirrer and placed into glass hypovials with Teflon-lined septa, and stored at 4°C.

About six blanks were prepared at the start of each sample analysis day by filling 18 mL hypovials with organic-free water and capping with Teflon-faced septa and aluminum crimp seals. They were solvent extracted and analyzed periodically throughout the day to check for lab contamination. Blank data are provided in Tables D-2 to D-7.

The method detection limits (MDL) for the compounds were determined using an EPA method which defines the MDL as the minimum concentration measurable with a 99% confidence that it is greater than zero. Method detection limits for the monoaromatics ranged from 0.6 to 1.8 ug/L (Table D-1).

Table D-2. Blank Data for the First Sample Round

SNAPSHOT 1 - SHIMADZU #1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	19-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	19-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	19-Jul-88	0.0	3.1	0.0	0.0	0.0	0.0
MAX.		0.0	3.1	0.0	0.0	0.0	0.0
AVG.		0.0	1.0	0.0	0.0	0.0	0.0
B1	20-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	20-Jul-88	0.0	3.3	0.0	0.0	0.0	0.0
B3	20-Jul-88	0.0	3.1	0.0	0.0	0.0	0.0
MAX.		0.0	3.3	0.0	0.0	0.0	0.0
AVG.		0.0	2.1	0.0	0.0	0.0	0.0
B1	21-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	21-Jul-88	0.0	2.2	0.0	0.0	0.0	0.0
B3	21-Jul-88	0.0	3.0	0.0	0.0	0.0	0.0
MAX.		0.0	3.0	0.0	0.0	0.0	0.0
AVG.		0.0	1.7	0.0	0.0	0.0	0.0
B4	22-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0

Table D-2. Continued

SNAPSHOT 1 - SHIMADZU #1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	25-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B1	27-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	27-Jul-88	0.0	2.6	0.0	0.0	0.0	0.0
MAX.		0.0	2.6	0.0	0.0	0.0	0.0
AVG.		0.0	1.3	0.0	0.0	0.0	0.0
B1	28-Jul-88	0.0	1.9	0.0	0.0	0.0	0.0
B2	28-Jul-88	25.5	6.7	0.0	0.0	0.0	0.0
B3	28-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		25.5	6.7	0.0	0.0	0.0	0.0
AVG.		8.5	2.9	0.0	0.0	0.0	0.0
B1	29-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	29-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	02-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	02-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	03-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	03-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B2	04-Aug-88	7.3	0.0	0.0	0.0	0.0	0.0

Table D-2. Continued

SNAPSHOT 1 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	19-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	19-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	19-Jul-88	0.0	1.3	4.0	0.0	0.0	0.0
MAX.		0.0	1.3	4.0	0.0	0.0	0.0
AVG.		0.0	0.4	1.3	0.0	0.0	0.0
B1	20-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	20-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	20-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	21-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	21-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	21-Jul-88	0.9	0.0	2.3	0.0	0.0	0.0
MAX.		0.9	0.0	2.3	0.0	0.0	0.0
AVG.		0.3	0.0	0.8	0.0	0.0	0.0
B4	22-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0

Table D-2. Continued

SNAPSHOT 1 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	25-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	25-Jul-88	0.0	0.0	2.0	0.0	0.0	0.0
*B2	25-Jul-88	0.0	5.2	6.2	4.0	7.0	6.6
MAX.		0.0	5.2	6.2	4.0	7.0	6.6
AVG.		0.0	1.7	2.7	1.3	2.3	2.2
B1	27-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	27-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	28-Jul-88	0.0	1.2	0.0	0.0	0.0	0.0
B2	28-Jul-88	0.0	2.4	0.0	0.0	0.0	0.0
MAX.		0.0	2.4	0.0	0.0	0.0	0.0
AVG.		0.0	1.8	0.0	0.0	0.0	0.0
B1	29-Jul-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	29-Jul-88	0.0	0.0	1.6	0.0	0.0	0.0
MAX.		0.0	0.0	1.6	0.0	0.0	0.0
AVG.		0.0	0.0	0.8	0.0	0.0	0.0
B1	02-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B1	03-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	03-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0

Table D-3. Blank Data for the Second Sample Round

SNAPSHOT 2 - SHIMADZU #1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	23-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	23-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	23-Aug-88	0.0	0.0	2.7	0.0	0.0	0.0
MAX.		0.0	0.0	2.7	0.0	0.0	0.0
AVG		0.0	0.0	0.9	0.0	0.0	0.0
B1	24-Aug-88	0.0	0.0	2.1	0.0	0.0	0.0
B2	24-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	24-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		0.0	0.0	2.1	0.0	0.0	0.0
AVG		0.0	0.0	0.7	0.0	0.0	0.0
B1	25-Aug-88	0.0	8.3	0.0	0.0	0.0	0.0
B2	25-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	25-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B4	25-Aug-88	0.0	0.0	2.1	0.0	0.0	0.0
B5	25-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		0.0	8.3	2.1	0.0	0.0	0.0
AVG		0.0	1.7	0.4	0.0	0.0	0.0
B1	26-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	26-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		0.0	0.0	0.0	0.0	0.0	0.0
AVG		0.0	0.0	0.0	0.0	0.0	0.0
B1	29-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	29-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	29-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B4	29-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		0.0	0.0	0.0	0.0	0.0	0.0
AVG		0.0	0.0	0.0	0.0	0.0	0.0

Table D-3. Continued

SNAPSHOT 2 - SHIMADZU #1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	30-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	30-Aug-88	7.4	6.9	6.6	6.1	1.7	6.6
MAX		7.4	6.9	6.6	6.1	1.7	6.6
AVG		3.7	3.4	3.3	3.0	0.9	3.3
B1	31-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	31-Aug-88	1.8	0.0	0.0	0.0	0.0	0.0
B3	31-Aug-88	5.0	0.0	0.0	0.0	0.0	0.0
B4	31-Aug-88	6.4	0.0	0.0	0.0	0.0	0.0
B5	31-Aug-88	3.8	0.0	0.0	0.0	0.0	0.0
MAX		6.4	0.0	0.0	0.0	0.0	0.0
AVG		3.4	0.0	0.0	0.0	0.0	0.0
B1	01-Sep-88	4.6	0.0	0.0	0.0	0.0	0.0
B2	01-Sep-88	4.7	0.0	0.0	0.0	0.0	0.0
B3	01-Sep-88	13.3	0.0	0.0	0.0	0.0	0.0
MAX		13.3	0.0	0.0	0.0	0.0	0.0
AVG		7.5	0.0	0.0	0.0	0.0	0.0
B1	02-Sep-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	02-Sep-88	9.7	0.0	0.0	0.0	0.0	0.0
MAX		9.7	0.0	0.0	0.0	0.0	0.0
AVG		4.9	0.0	0.0	0.0	0.0	0.0
B1	06-Sep-88	4.3	0.0	0.0	0.0	0.0	0.0
B2	06-Sep-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		4.3	0.0	0.0	0.0	0.0	0.0
AVG		2.2	0.0	0.0	0.0	0.0	0.0
B3	07-Sep-88	0.0	2.1	3.3	0.0	0.0	0.0

Table D-3. Continued

SNAPSHOT 2 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	23-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	23-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	23-Aug-88	0.0	0.0	1.9	0.0	0.0	0.0
MAX		0.0	0.0	1.9	0.0	0.0	0.0
AVG		0.0	0.0	0.6	0.0	0.0	0.0
B1	24-Aug-88	0.0	0.6	2.6	0.0	0.0	0.0
B2	24-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		0.0	0.6	2.6	0.0	0.0	0.0
AVG		0.0	0.3	1.3	0.0	0.0	0.0
B1	25-Aug-88	0.0	0.0	2.1	0.0	0.0	0.0
B2	25-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	25-Aug-88	8.0	6.5	0.0	0.0	0.0	0.0
B4	25-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B5	25-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		8.0	6.5	2.1	0.0	0.0	0.0
AVG		1.6	1.3	0.4	0.0	0.0	0.0
B1	26-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	26-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		0.0	0.0	0.0	0.0	0.0	0.0
AVG		0.0	0.0	0.0	0.0	0.0	0.0
B1	29-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	29-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	29-Aug-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		0.0	0.0	0.0	0.0	0.0	0.0
AVG		0.0	0.0	0.0	0.0	0.0	0.0

Table D-4. Blank Data for the Third Sample Round

SNAPSHOT 3 - SHIMADZU #1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	27-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	27-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	28-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	28-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	28-Oct-88	9.2	0.0	0.0	0.0	0.0	0.0
MAX		9.2	0.0	0.0	0.0	0.0	0.0
AVG.		3.1	0.0	0.0	0.0	0.0	0.0
B1	31-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	31-Oct-88	0.0	0.0	4.1	0.0	0.0	0.0
B3	31-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX		0.0	0.0	4.1	0.0	0.0	0.0
AVG.		0.0	0.0	1.4	0.0	0.0	0.0
B1	01-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	01-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	01-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B4	01-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B5	01-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B6	01-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	02-Nov-88	4.7	2.1	0.0	0.0	0.0	0.0
B2	02-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	02-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B4	02-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		4.7	2.1	0.0	0.0	0.0	0.0
AVG.		1.2	0.5	0.0	0.0	0.0	0.0
B1	03-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	03-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	03-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0 0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0

Table D-4. Continued

SNAPSHOT 3 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	25-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	25-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	26-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	26-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	26-Oct-88	0.0	1.5	0.0	0.0	0.0	0.0
MAX.		0.0	1.5	0.0	0.0	0.0	0.0
AVG.		0.0	0.5	0.0	0.0	0.0	0.0
B1	27-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	27-Oct-88	0.0	0.0	2.3	0.0	0.0	0.0
MAX.		0.0	0.0	2.3	0.0	0.0	0.0
AVG.		0.0	0.0	1.1	0.0	0.0	0.0
B1	28-Oct-88	0.0	1.7	0.0	0.0	0.0	0.0
B2	28-Oct-88	0.0	3.7	2.3	0.0	0.0	0.0
B3	28-Oct-88	0.0	2.2	1.8	0.0	0.0	0.0
MAX.		0.0	3.7	2.3	0.0	0.0	0.0
AVG.		0.0	2.6	1.4	0.0	0.0	0.0

Table D-4. Continued

SNAPSHOT 3 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	31-Oct-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	31-Oct-88	0.0	1.6	2.6	0.0	0.0	0.0
B3	31-Oct-88	3.5	0.0	0.0	0.0	0.0	0.0
MAX.		3.5	1.6	2.6	0.0	0.0	0.0
AVG.		1.2	0.5	0.9	0.0	0.0	0.0
B1	01-Nov-88	2.8	0.0	0.0	0.0	0.0	0.0
B2	01-Nov-88	1.4	0.0	2.0	0.0	0.0	0.0
B3	01-Nov-88	19.8	1.5	0.0	0.0	0.0	0.0
B4	01-Nov-88	0.0	1.1	0.0	0.0	0.0	0.0
B5	01-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B6	01-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		19.8	1.5	2.0	0.0	0.0	0.0
AVG.		4.0	0.4	0.3	0.0	0.0	0.0
B1	02-Nov-88	0.0	2.9	0.0	0.0	0.0	0.0
B2	02-Nov-88	0.0	2.8	0.0	0.0	0.0	0.0
B3	02-Nov-88	0.0	1.3	0.0	0.0	0.0	0.0
B4	02-Nov-88	0.0	2.3	0.0	0.0	0.0	0.0
B5	02-Nov-88	0.0	1.6	0.0	0.0	0.0	0.0
MAX.		0.0	2.9	0.0	0.0	0.0	0.0
AVG.		0.0	2.2	0.0	0.0	0.0	0.0
B1	03-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B2	03-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
B3	03-Nov-88	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0

Table D-5. Blank Data for the Fourth Sample Round

SNAPSHOT 4 - SHIMADZU #1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	01-Jun-89	1.0	1.0	0.0	0.0	0.0	0.0
B2	01-Jun-89	3.0	0.0	0.0	0.0	0.0	0.0
B3	01-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	01-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		3.0	1.0	0.0	0.0	0.0	0.0
AVG.		1.0	0.3	0.0	0.0	0.0	0.0
B1	02-Jun-89	1.4	0.0	0.0	0.0	0.0	0.0
B2	02-Jun-89	0.7	0.8	0.0	0.0	0.0	0.0
B3	02-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		1.4	0.8	0.0	0.0	0.0	0.0
AVG.		0.7	0.3	0.0	0.0	0.0	0.0
B1	05-Jun-89	0.0	1.5	0.0	0.0	0.0	0.0
B2	05-Jun-89	1.3	2.2	0.0	0.0	0.0	0.0
B3	05-Jun-89	0.0	0.9	0.0	0.0	0.0	0.0
B4	05-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	05-Jun-89	2.6	0.0	0.0	0.0	0.0	0.0
MAX.		2.6	2.2	0.0	0.0	0.0	0.0
AVG.		0.8	0.9	0.0	0.0	0.0	0.0
B1	06-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	06-Jun-89	0.0	0.0	3.7	0.0	0.0	0.0
B3	06-Jun-89	0.0	2.0	0.0	0.0	0.0	0.0
B4	06-Jun-89	0.0	0.0	4.0	0.0	0.0	0.0
MAX.		0.0	2.0	4.0	0.0	0.0	0.0
AVG.		0.0	0.5	1.9	0.0	0.0	0.0
B1	07-Jun-89	1.6	1.7	3.3	0.0	0.0	0.0
B2	07-Jun-89	1.0	1.6	5.9	0.0	0.0	0.0
MAX.		1.6	1.7	5.9	0.0	0.0	0.0
AVG.		1.3	1.7	4.6	0.0	0.0	0.0
B1	08-Jun-89	1.7	3.1	6.5	0.0	0.0	0.0
B1	06-Jul-89	0.0	1.7	0.0	0.0	0.0	0.0

Table D-5. Continued

SNAPSHOT 4 - SHIMADZU #1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	25-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	25-May-89	0.0	3.9	0.0	0.0	0.0	0.0
B3	25-May-89	2.5	2.8	4.7	0.0	0.0	0.0
B4	25-May-89	0.0	3.2	6.4	0.0	0.0	0.0
MAX.		2.5	3.9	6.4	0.0	0.0	0.0
AVG.		0.6	2.5	2.8	0.0	0.0	0.0
B1	26-May-89	0.0	6.4	0.0	0.0	0.0	0.0
B2	26-May-89	0.0	4.0	0.0	0.0	0.0	0.0
B3	26-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	26-May-89	0.0	1.0	0.0	0.0	0.0	0.0
MAX.		0.0	6.4	0.0	0.0	0.0	0.0
AVG.		0.0	2.8	0.0	0.0	0.0	0.0
B1	29-May-89	0.0	5.0	5.9	0.0	0.0	0.0
B2	29-May-89	2.9	0.0	7.1	0.0	0.0	0.0
B3	29-May-89	0.0	0.0	3.9	0.0	0.0	0.0
B4	29-May-89	1.3	1.0	6.7	0.0	0.0	0.0
B5	29-May-89	1.8	2.0	6.9	0.0	0.0	0.0
MAX.		2.9	5.0	7.1	0.0	0.0	0.0
AVG.		1.2	1.6	6.1	0.0	0.0	0.0
B1	30-May-89	0.0	0.6	1.7	0.0	0.0	3.2
B2	30-May-89	1.9	0.0	6.3	0.0	0.0	0.0
B3	30-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	30-May-89	0.0	0.0	5.9	0.0	0.0	0.0
MAX.		1.9	0.6	6.3	0.0	0.0	3.2
AVG.		0.5	0.2	3.5	0.0	0.0	0.8
B1	31-May-89	1.0	1.7	3.9	4.4	5.1	4.9
B2	31-May-89	1.3	0.9	0.0	0.0	0.0	0.0
B3	31-May-89	0.0	1.8	0.0	0.0	0.0	0.0
B4	31-May-89	0.0	0.5	0.5	0.0	0.0	0.0
B5	31-May-89	0.0	6.3	0.0	0.0	0.0	0.0
MAX.		1.3	6.3	3.9	4.4	5.1	4.9
AVG.		0.5	2.2	0.9	0.9	1.0	1.0

Table D-5. Continued

SNAPSHOT 4 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	25-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	25-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	25-May-89	0.0	1.9	1.9	0.0	0.0	0.0
B4	25-May-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	1.9	1.9	0.0	0.0	0.0
AVG.		0.0	0.5	0.5	0.0	0.0	0.0
B1	26-May-89	0.0	5.1	0.0	0.0	0.0	0.0
B2	26-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	26-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	26-May-89	0.0	5.2	0.0	0.0	0.0	0.0
MAX.		0.0	5.2	0.0	0.0	0.0	0.0
AVG.		0.0	3.4	0.0	0.0	0.0	0.0
B1	29-May-89	0.0	4.9	2.6	0.0	0.0	0.0
B2	29-May-89	0.0	5.5	6.8	0.0	0.0	0.0
B3	29-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	29-May-89	0.0	4.1	5.5	0.0	0.0	0.0
B5	29-May-89	0.0	3.5	4.8	0.0	0.0	0.0
MAX.		0.0	5.5	6.8	0.0	0.0	0.0
AVG.		0.0	3.6	3.9	0.0	0.0	0.0
B1	30-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	30-May-89	0.0	5.1	2.5	0.0	0.0	0.0
B3	30-May-89	0.0	2.7	0.0	0.0	0.0	0.0
B4	30-May-89	0.0	2.8	2.2	0.0	0.0	0.0
MAX.		0.0	5.1	2.5	0.0	0.0	0.0
AVG.		0.0	2.6	1.2	0.0	0.0	0.0
B1	31-May-89						
B2	31-May-89	0.0	3.1	0.0	0.0	0.0	0.0
B3	31-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	31-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	31-May-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	3.1	0.0	0.0	0.0	0.0
AVG.		0.0	0.8	0.0	0.0	0.0	0.0
B1	01-Jun-89	0.0	1.2	0.0	0.0	0.0	0.0
B2	01-Jun-89	0.0	7.0	0.0	0.0	0.0	0.0
B3	01-Jun-89	0.0	0.2	0.0	0.0	0.0	0.0
B4	01-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	7.0	0.0	0.0	0.0	0.0
AVG.		0.0	2.1	0.0	0.0	0.0	0.0

Table D-5. Continued

SNAPSHOT 4 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	02-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	02-Jun-89	0.0	0.8	0.0	0.0	0.0	0.0
B3	02-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.8	0.0	0.0	0.0	0.0
AVG.		0.0	0.3	0.0	0.0	0.0	0.0
B1	05-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	05-Jun-89	0.0	0.0	0.0	0.0	0.0	0.9
B3	05-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	05-Jun-89	0.0	0.0	0.4	0.5	0.6	0.0
B5	05-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.4	0.5	0.6	0.9
AVG.		0.0	0.0	0.1	0.1	0.1	0.2
B1	06-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	06-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	06-Jun-89	0.0	0.0	0.0	0.0	0.4	0.9
B4	06-Jun-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.4	0.9
AVG.		0.0	0.0	0.0	0.0	0.1	0.2
B1	07-Jun-89	0.0	0.0	4.2	0.0	0.0	0.0
B2	07-Jun-89	0.0	0.0	6.2	0.0	0.0	0.0
MAX.		0.0	0.0	6.2	0.0	0.0	0.0
AVG.		0.0	0.0	5.2	0.0	0.0	0.0
SNAPSHOT 4 - HP 5890							
B1	30-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	30-May-89	0.0	7.1	0.0	0.0	0.0	0.0
B3	30-May-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	30-May-89	0.0	6.8	0.0	0.0	0.0	0.0
B5	30-May-89	0.0	8.0	9.7	0.0	0.0	0.0
B6	30-May-89	0.0	7.8	11.0	0.0	0.0	0.0
MAX.		0.0	8.0	11.0	0.0	0.0	0.0
AVG.		0.0	4.9	3.4	0.0	0.0	0.0

Table D-6. Blank Data for the Fifth Sample Round

SNAPSHOT 5 - SHIMADZU #1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	15-Aug-89	0.0	0.0	7.3	0.0	0.0	0.0
B2	15-Aug-89	0.0	0.0	9.0	0.0	0.0	0.0
B3	15-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	15-Aug-89	0.0	0.0	5.9	0.0	0.0	0.0
MAX.		0.0	0.0	9.0	0.0	0.0	0.0
AVG.		0.0	0.0	5.5	0.0	0.0	0.0
B1	16-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	16-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	16-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	16-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	16-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	17-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	17-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	17-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	17-Aug-89	0.0	0.0	5.0	0.0	0.0	0.0
B5	17-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	5.0	0.0	0.0	0.0
AVG.		0.0	0.0	1.0	0.0	0.0	0.0
B1	18-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	18-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	18-Aug-89	0.0	0.0	3.4	0.0	0.0	0.0
MAX.		0.0	0.0	3.4	0.0	0.0	0.0
AVG.		0.0	0.0	1.1	0.0	0.0	0.0
B1	21-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	21-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	21-Aug-89	0.0	0.0	5.4	0.0	0.0	0.0
B4	21-Aug-89	0.0	0.0	6.9	0.0	0.0	0.0
B5	21-Aug-89	0.0	0.0	6.5	0.0	0.0	0.0
MAX.		0.0	0.0	6.9	0.0	0.0	0.0
AVG.		0.0	0.0	3.8	0.0	0.0	0.0

Table D-6. Continued

SNAPSHOT 5 - SHIMADZU #1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	22-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	22-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	22-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	22-Aug-89	0.0	0.0	5.7	0.0	0.0	0.0
B5	22-Aug-89	0.0	0.0	6.3	0.0	0.0	0.0
MAX.		0.0	0.0	6.3	0.0	0.0	0.0
AVG.		0.0	0.0	2.4	0.0	0.0	0.0
B1	23-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	23-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	24-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	24-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	24-Aug-89	0.0	1.3	0.0	0.0	0.0	0.0
MAX.		0.0	1.3	0.0	0.0	0.0	0.0
AVG.		0.0	0.4	0.0	0.0	0.0	0.0
B1	25-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	25-Aug-89	0.0	2.3	0.0	0.0	0.0	0.0
B3	25-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	2.3	0.0	0.0	0.0	0.0
AVG.		0.0	0.8	0.0	0.0	0.0	0.0
B1	28-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	28-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	28-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	28-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	28-Aug-89	0.0	0.0	8.3	0.0	0.0	0.0
MAX.		0.0	0.0	8.3	0.0	0.0	0.0
AVG.		0.0	0.0	1.7	0.0	0.0	0.0
B1	29-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	29-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	29-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	29-Aug-89	0.0	0.0	6.0	0.0	0.0	0.0
B5	29-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	6.0	0.0	0.0	0.0
AVG.		0.0	0.0	1.2	0.0	0.0	0.0

Table D-6. Continued

SNAPSHOT 5 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	15-Aug-89	0.0	0.0	7.3	0.0	0.0	0.0
B2	15-Aug-89	0.0	0.0	6.7	0.0	0.0	0.0
B3	15-Aug-89	0.0	0.0	1.7	0.0	0.0	0.0
B4	15-Aug-89	0.0	0.0	5.2	0.0	0.0	0.0
MAX.		0.0	0.0	7.3	0.0	0.0	0.0
AVG.		0.0	0.0	5.2	0.0	0.0	0.0
B1	16-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	16-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	16-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	16-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	17-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	17-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	17-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	17-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	17-Aug-89	0.0	0.0	2.7	0.0	0.0	0.0
MAX.		0.0	0.0	2.7	0.0	0.0	0.0
AVG.		0.0	0.0	0.5	0.0	0.0	0.0
B1	18-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	18-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	18-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	18-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	21-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	21-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	21-Aug-89	0.0	0.0	5.4	0.0	0.0	0.0
B4	21-Aug-89	0.0	0.0	3.9	0.0	0.0	0.0
B5	21-Aug-89	0.0	0.0	5.1	0.0	0.0	0.0
MAX.		0.0	0.0	5.4	0.0	0.0	0.0
AVG.		0.0	0.0	2.9	0.0	0.0	0.0

Table D-6. Continued

SNAPSHOT 5 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	22-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	22-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	22-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	22-Aug-89	0.0	0.0	2.7	0.0	0.0	0.0
B5	22-Aug-89	0.0	0.0	4.8	0.0	0.0	0.0
MAX.		0.0	0.0	4.8	0.0	0.0	0.0
AVG.		0.0	0.0	1.5	0.0	0.0	0.0
B1	23-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	23-Aug-89	0.0	0.0	1.7	0.0	0.0	0.0
MAX.		0.0	0.0	1.7	0.0	0.0	0.0
AVG.		0.0	0.0	0.9	0.0	0.0	0.0
B1	24-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	24-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	24-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	25-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	25-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	28-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	28-Aug-89	0.0	0.0	5.6	0.0	0.0	0.0
B3	28-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	28-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	28-Aug-89	0.0	0.0	9.1	0.0	0.0	3.6
MAX.		0.0	0.0	9.1	0.0	0.0	3.6
AVG.		0.0	0.0	2.9	0.0	0.0	0.7
B1	29-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	29-Aug-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	29-Aug-89	0.0	0.0	0.0	0.0	0.0	1.2
B4	29-Aug-89	0.0	0.0	5.4	0.0	0.0	0.0
B5	29-Aug-89	0.0	0.0	3.2	0.0	0.0	0.0
MAX.		0.0	0.0	5.4	0.0	0.0	1.2
AVG.		0.0	0.0	1.7	0.0	0.0	0.2

Table D-7. Blank Data for the Sixth Sample Round

SNAPSHOT 6 - SHIMADZU 1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	31-Oct-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	31-Oct-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	31-Oct-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	31-Oct-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	31-Oct-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B6	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	02-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	02-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	02-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	03-Nov-89	0.0	1.8	0.0	0.0	0.0	0.0
B2	03-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	03-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	03-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	03-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	1.8	0.0	0.0	0.0	0.0
AVG.		0.0	0.4	0.0	0.0	0.0	0.0
B1	06-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	06-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	06-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	06-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0

Table D-7. Continued

SNAPSHOT 6 - SHIMADZU 1

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	07-Nov-89	0.0	10.9	0.0	0.0	0.0	0.0
B2	07-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	07-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	07-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	07-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	10.9	0.0	0.0	0.0	0.0
AVG		0.0	2.2	0.0	0.0	0.0	0.0
B1	08-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	08-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	08-Nov-89	0.0	1.9	0.0	0.0	0.0	0.0
B4	08-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	1.9	0.0	0.0	0.0	0.0
AVG		0.0	0.5	0.0	0.0	0.0	0.0
B1	10-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	10-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	13-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	13-Nov-89	0.0	0.0	3.9	0.0	0.0	0.0
B4	13-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	13-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	3.9	0.0	0.0	0.0
AVG.		0.0	0.0	1.0	0.0	0.0	0.0
B1	13-Nov-89	0.0	1.6	0.0	0.0	0.0	0.0
B2	14-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	1.6	0.0	0.0	0.0	0.0
AVG.		0.0	0.8	0.0	0.0	0.0	0.0

Table D-7. Continued

SNAPSHOT 6 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	31-Oct-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	31-Oct-89	0.0	0.0	0.3	0.0	0.0	0.0
B3	31-Oct-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	31-Oct-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	31-Oct-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.3	0.0	0.0	0.0
AVG.		0.0	0.0	0.1	0.0	0.0	0.0
B1	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	01-Nov-89	2.7	1.6	0.0	0.0	0.0	0.0
B6	01-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		2.7	1.6	0.0	0.0	0.0	0.0
AVG.		0.5	0.3	0.0	0.0	0.0	0.0
B1	02-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	02-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	02-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	02-Nov-89	0.0	0.7	0.0	0.0	0.0	0.0
B5	02-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.7	0.0	0.0	0.0	0.0
AVG.		0.0	0.1	0.0	0.0	0.0	0.0
B1	03-Nov-89	1.2	0.0	0.0	0.0	0.0	0.0
B2	03-Nov-89	0.0	0.8	1.4	0.0	0.0	0.0
B3	03-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	03-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	03-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		1.2	0.8	1.4	0.0	0.0	0.0
AVG.		0.2	0.2	0.3	0.0	0.0	0.0
B1	06-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	06-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	06-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	06-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0

Table D-7. Continued

SNAPSHOT 6 - SHIMADZU #2

BLANK NUMBER	DATE ANALYZED	BENZENE (ug/L)	TOLUENE (ug/L)	ET-BENZ (ug/L)	P-XYLENE (ug/L)	M-XYLENE (ug/L)	O-XYLENE (ug/L)
B1	07-Nov-89	0.0	1.3	1.2	0.0	0.0	0.0
B2	07-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	07-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	07-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B5	07-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	1.3	1.2	0.0	0.0	0.0
AVG.		0.0	0.3	0.2	0.0	0.0	0.0
B1	08-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	08-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	08-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	08-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	09-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	09-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	09-Nov-89	2.6	5.2	3.4	1.4	0.0	0.0
B4	09-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		2.6	5.2	3.4	1.4	0.0	0.0
AVG.		0.6	1.3	0.9	0.3	0.0	0.0
B1	10-Nov-89	0.0	0.9	0.0	0.0	0.0	0.0
B2	10-Nov-89	0.0	0.0	7.7	0.0	0.0	0.0
MAX.		0.0	0.9	7.7	0.0	0.0	0.0
AVG.		0.0	0.4	3.9	0.0	0.0	0.0
B1	13-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	13-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B3	13-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B4	13-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0
B1	13-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
B2	14-Nov-89	0.0	0.0	0.0	0.0	0.0	0.0
MAX.		0.0	0.0	0.0	0.0	0.0	0.0
AVG.		0.0	0.0	0.0	0.0	0.0	0.0

D.2 Oxygenates

The 1 mL sample set aside after sample extraction for the monoaromatics was analyzed for methanol and MTBE by direct aqueous injection into a gas chromatograph. A 4 microliter aliquot of each sample was removed using a syringe equipped with a Cheney adapter, and injected into a Hewlett Packard 5840 A gas chromatograph with a flame ionization detector. Operating conditions for the gas chromatograph are shown in Table D-8. Detection limits of about 100 ug/L for methanol and 250 ug/L for MTBE were determined by the EPA method.

Table D-8. Analytical Information for the Oxygenates.

GC Column Temperatures (Isothermal)

Oxygenate	Column Temp. °C	Retention Time
Methanol	100	1.4
MTBE	190	3.0

Method Detection Limits

Oxygenate	N	X (mg/L)	Xo (mg/L)	S%	E%	MDL (mg/L)
Methanol	12	.760+/-.039	.988	5.13	-23.1	.106
MTBE	12	.533+/-.093	.740	17.4	-28.0	.249

Accuracy and Precision at Typical Concentration

Oxygenate	N	X (mg/L)	Xo (mg/L)	S%	E%
Methanol	21	409.92+/-8.73	395.0	2.13	+3.78
MTBE	21	71.95+/-1.31	74.0	1.81	-2.77

N : number of replicate determinations
X : mean of replicate determinations, 99% confidence level
Xo : true value
S% : relative standard deviation
E% : relative error
MDL: method detection limit

D.3 Chloride

Chloride samples were analyzed by an automated wet chemical procedure described by Patrick *et al.* (1986), on a Technicon Autoanalyzer II. The method (Technicon Industrial Method No. 99-70 W/B), involves release of thiocyanate ions into solution in proportion to the concentration of chloride in the sample. In the presence of ferric ions, a highly colored solution forms which can be quantified using spectrophotometry. The method is particularly effective for studies such as this in which the range of chloride concentrations in the samples is known in advance. The detection limit for this study was 1.5 mg/L.

For the last sampling round, a series of blind controls was included with the group of field samples to be analyzed for chloride. Two of the blind controls contained no chloride, and eleven were spiked with 20.45 mg/L of chloride. Results of the analysis of the blind controls are provided in Table D-9. Both blanks were reported at the detection limit of 1.5 mg/L, the relative standard deviation of the chloride concentration in the blind controls was 8%, and the mean of the blind controls (20.22) was within 1% of the true value.

Table D-9. Results from the Day 476 Chloride Blind Controls

Sample Number	Spiked controls (mg/L)	Sample Number	Blanks (mg/L)
641-4	20.2	732-16	1.52
668-4	21.3	718-17	1.50
680-3	23.2		
680-4	19.2		
698-12	17.8		
708-16	19.5		
717-16	18.5		
718-16	20.1		
731-16	19.4		
750-12	21.4		
750-4	21.4		
True Value	20.45		<1.5
Mean	20.22		1.51
Variance	2.69		-
Standard Deviation	1.64		-
Relative Stand. Dev.	8.11%		-

D.4 Dissolved Oxygen

Each dissolved oxygen sample was analyzed at the field site using the azide-modified Winkler titration technique. The method is described in detail by APHA *et al.* (1985). Analyses were done under the shade of a tarp to avoid exposure of the samples and reagents to sunlight. Reagents were added directly to the 50 mL glass syringes in which the samples had been collected in order to reduce the chances of exposure to atmospheric oxygen.

A 0.5 mL aliquot of manganous sulphate solution was added to each sample, and the syringe was sealed and shaken. A 0.5 mL aliquot of alkali-iodide-azide reagent was then added and the sample was mixed by inverting 15 times. The flocculent was allowed to settle to half the sample volume, and then the sample was mixed again and permitted to settle. A 0.5 mL aliquot of phosphoric acid was added, and the sample was transferred to a 125 mL erlenmeyer flask. The sample was titrated using a standardized 0.0025 N sodium thiosulphate solution. Starch was added as an endpoint indicator. The detection limit for this method is 0.2 - 0.6 mg/L.

D.5 References

APHA, AWWA and WPCF, 1985. *Standard Methods for the Examination of Water and Wastewater.* M.A.H. Franson (manag. ed.), APHA, Washington D.C.

Patrick, G.C., J.F. Barker, R.W. Gillham, C.I. Mayfield, and D. Major, 1986. *The Behavior of Soluble Petroleum Product-Derived Hydrocarbons in Groundwater.* PACE Phase II Report 86-1. Petroleum Association for the Conservation of the Canadian Environment.

APPENDIX E

SURFACE II PARAMETERS

Contents:

Tables:

The Surface II contouring package of Sampson (1978) was used to project the vertically integrated concentration data to a regular grid. The input files to the Surface II program consist of the X and Y coordinates and the vertically integrated concentration data for each multilevel piezometer, and data files are prepared separately for each plume. This Appendix describes the interpolation options in the package and the rationale for parameter selection. The data for each snapshot are available separately from API.

E.1 Search Routine Options

The interpolation procedure begins with a nearest neighbor search routine. The search method chosen for this study finds the four nearest neighboring data points, regardless of their angular distribution around the point being estimated. The maximum search radius is a function of the piezometer spacing. A search for four nearest neighbors was specified to ensure that the search radius would not be disproportionately large relative to the size of the solute plumes and the expected correlation lengths of the concentration data. Freyberg (1986), in a previous tracer test at the site, noted that the vertical distributions of chloride concentration were consistent from sampler to sampler over horizontal distances of three to four meters. This finding is consistent with the scale of structural bedding in the aquifer. Maximum search radii calculated by the program for the runs of this study are tabulated in Table E-1, and they typically ranged from three to four meters.

Table E-1. Maximum Search Radii Calculated for each Snapshot.

Sample Round	Maximum Search Radius
1	3.059
2	3.753
3	3.338
4	3.825
5	4.370
6	4.607

E.2 Interpolation and Weighting Options

Once the nearest neighbors are located, the grid node value is estimated by interpolation. Two interpolation options are available, a slope projection option (option 1) and a weighted averaging option (option 0). The first is a two-phase weighted averaging of the projected slopes from the nearest neighboring data points around each grid node. This method does not preserve the original data range and tends to create spurious highs or lows. The second is a distance weighted averaging of surrounding control points. Option 0 preserves the original data range. It should be noted, however, that the Surface II package does not preserve the original data: the end result of the areal interpolation routine is a regular grid of depth integrated concentrations, all of which are estimates.

Five weighting options are available in the package: they are listed in Table D-2. Options 0 and 1 place the least weight on the known data points, while option 4 weights the data points most heavily. All of the weighting options are available for each interpolation option, yielding a total of ten possible combinations, each of which will create a different grid from the same data file.

Table E-2. Weighting Options Available in Surface II.

Option	Weighting Function
0	$\frac{(1-D/1.1*D_{(max)})^2}{(D/1.1*D_{(max)})^2}$
1	1/D
2	1/D2
3	1/D4
4	1/D6

E.3 Grid Size and Plume Boundaries

The solute data to be projected to a regular grid must be bounded by sufficient zero values to ensure that the shape of the plume is preserved. Although the plumes were consistently bounded by piezometers with zero values, they were not always closely spaced around the

plume boundaries, and it was necessary to add ficticious zero-value control points to the integrated data files to ensure that the gridded data would be representative.

Some discretion was necessary in choosing locations for the points: if they were too closely spaced, grid nodes in other portions of the grid would fail the search routines. Judgments on placement of the ficticious zero values were made based on the hand-contoured depth integrated data. An iterative approach was used: contour plots of the gridded data were made using the Surface II contouring package and compared to the contour plots of the true data in order to assess the appropriateness of placement of the zero-values. The grid size was chosen based on the areal extent of the solute plume being estimated. It simply represented a rectangular box that was large enough to encompass both the solute plumes and the surrounding zero-value control points.

E.4 Parameter Selection

In order to choose optimal parameters for running the field plumes through the Surface II gridding procedure, ficticious plumes of known mass were generated for the PS-6 chloride plume at each sample time. The ficticious plumes were run through the programs for each of the ten combinations of interpolation and weighting options for two or three grid spacings. Optimal parameters identified for each sample round are listed in Table E-3.

Table E-3. Surface II Parameters Selected for Each Sample Round

Snapshot	Interpolation option	Grid Node Spacing	Fraction of Piezometer Spacing
1	0-4	0.202	0.25
2	0-4	0.258	0.25
3	0-4	0.260	0.20
4	0-4	0.467	0.20
5	0-4	0.922	0.35
6	0-1	0.677	0.20

The grid node spacings chosen for the interpolation procedures depended on the piezometer spacing for the solute plume under analysis. In general, grid node spacings that represented one fifth to one third of the average piezometer spacing were selected. Thus, plumes situated in portions of the monitoring network with a wide piezometer spacing were projected to a coarser grid than those situated in denser portions of the monitoring network. This approach is similar to that taken by Freyberg (1986), but differs from that used by Berry-Spark (1987) and Patrick (1986), who retained identical grid node spacings for analysis of all solute plumes.

E.5 References

Sampson, R. J., 1978. *Surface II Graphics System, Revision One*. Kansas Geological Survey, Lawrence, Kansas, 240 pp.

APPENDIX F

LOCATIONS OF PLUME CROSS SECTIONS

This Appendix provides a key to samplers depicted in cross sections throughout the text. General cross section locations for each sample event are shown in map view, and samplers are listed by number as a key for individual Figures. For x and y coordinates of the samplers, see Appendix B, Table B-1.

Figures:

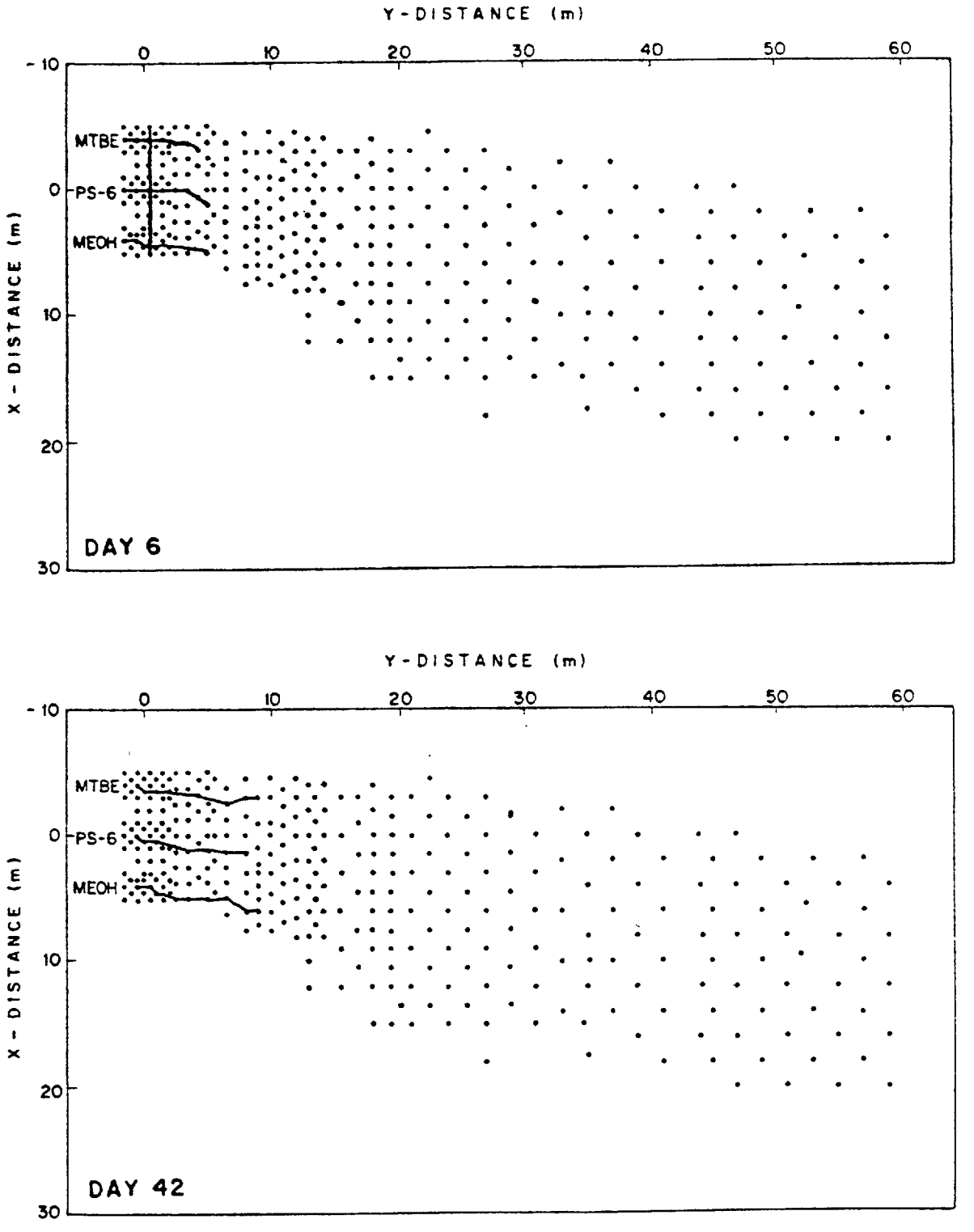

Figure F-1. Locations of cross sections taken through the plume centerlines for the first and second sample events.

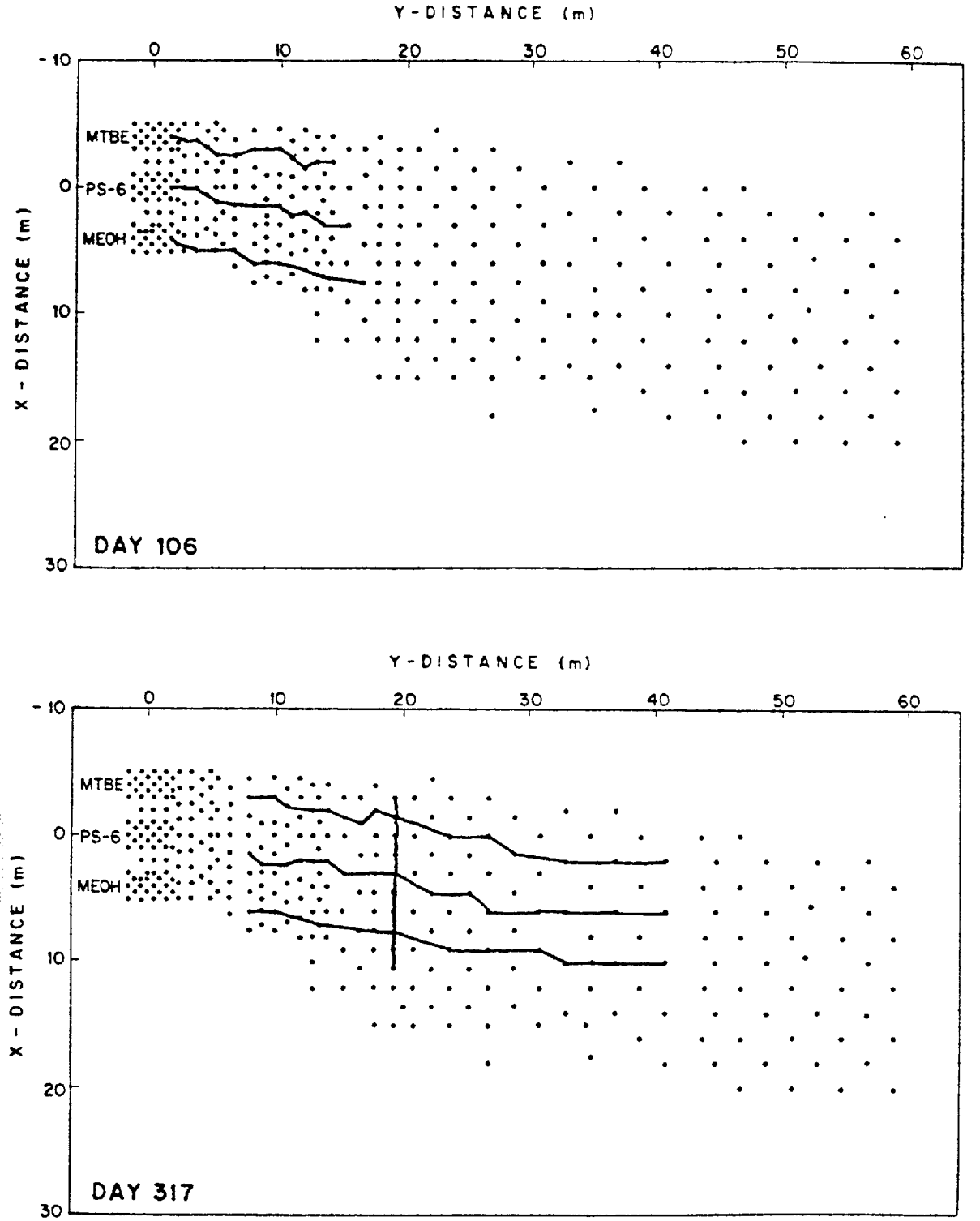

Figure F-2. Locations of cross sections taken through the plume centerlines for the third and fourth sample events.

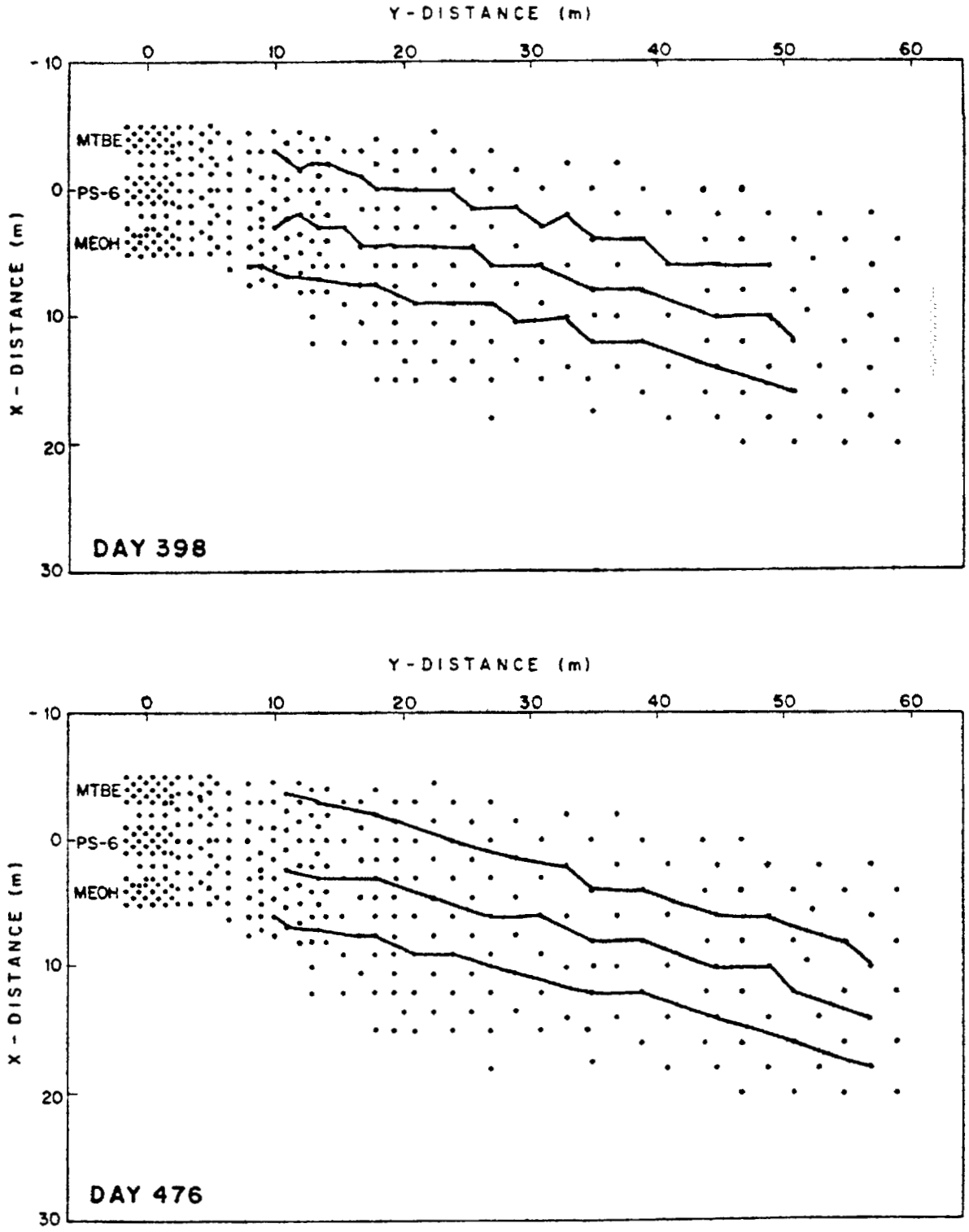

Figure F-3. Locations of cross sections taken through the plume centerlines for the fifth and sixth sample events.

WELLS INCLUDED IN CROSS SECTIONS:

Figure 2-2: Dissolved Oxygen

10% MTBE: N3-N3, N1-N4, OA-N4, 1-N4, 2-N3, 3-N3, 3A-N2
100% PS-6: N3-0, N1-0, OA-0, C15, 3-0, C20
85% Methanol: N3-3, N1-4, O-3, OB-3, 1A-3, 3-3

Figure 2-3: Dissolved Oxygen

OA-N5, OA-N4, OA-N3, OA-N2, OA-N1, OA-0, OA-1, OA-2, C5, C4, OA-5

Figure 5-7: Chloride

Day 106: 4-4, 5-4, 6-4, 6A-6, 7-4, 7B-4, 8A-4, 9B-3
Day 476: 17-4, 19-3, 20-4, 22-3, 23-4, 25-4, 27-4, 28-4, 30-4, 31-4

Figure 5-8: Day 317

Benzene: 6A-6, 7-4, 7B-4, 8A-4, 9B-3, 10-5, 11-5, 12-3, 13-3, 14-3, 16-3, 18-3, 19-3, 21-3
Chloride: 6A-6, 7-4, 7B-4, 8A-4, 9B-3, 10-5, 11-5, 12-3, 13-3, 14-3, 16-3, 18-3, 19-3, 21-3
Methanol: 4-4, 5-5, 6-4, 6A-6, 7-4, 7B-4, 8A-4, 9B-3, 10-5, 11-5, 12-3, 13-3, 14-3, 16-3, 18-3, 19-3, 21-3

Figure 5-9: Toluene

Day 106: 1-4, 1A-3, 4-4, 5-4, 6-4, 6A-6, 7-4, 7B-4, 8A-4, 9B-3
Day 398: 5-4, 6-4, 6A-6, 7A-5, 8A-4, 9B-3, 10-5, 12-3, 14-3, 16-3, 17-4, 19-3, 20-4

WELLS INCLUDED IN CROSS SECTIONS (continued)

Figure 5-10: p-Xylene

Day 398: 5-4, 6-4, 6A-6, 7A-5, 8A-4, 9B-3, 10-5, 12-3, 14-3, 16-3, 17-4, 19-3
Day 476: 7-4, 7A-5, 7B-4, 8A-4, 9B-3, 10-5, 11-5, 12-3, 14-3, 16-3, 17-4, 19-3

Figure 9-1: Dissolved Oxygen and Total BTEX, fourth sample round

11-N2, 11-N1, 11-0, 11-1, 11-2, 11-3, 11-4, 11-5, 11-6, 11-7

Figure 9-3: Dissolved Oxygen, Day 110

100% PS-6 Case: 1-0, 2-0, 3-0, C20, 4-1, 5-1, 6-1, 7-1, 7A-2, 7B-1, 8-1, 8B-1
85% Methanol Case: 1-4, 1A-3, C19, 5-4, 6-4, 6A-6, 7-4, 7B-4, 8A-3

Figure 9-4: Dissolved Oxygen, Day 321

100% PS-6 Case: 4-1, 5-1, 6-1, 6A-2, 7A-2, 7B-1, 8-1, 8B-1, 9-1, 10-2, 11-2, 12-1, 13-2, 15-2, 16-2, 18-2, 19-2, 21-2, 23-2

85% Methanol Case: 4-4, 5-4, 6-4, 6A-6, 7-4, 7B-4, 8A-4, 9B-3, 10-5, 11-5, 12-3, 13-3, 14-3, 16-3, 18-3, 19-3, 20-3, 21-3, 23-3

APPENDIX G

TRANSPORT AND FATE DATA

Tables:

Table G-1. Transport Calculations - 10% MTBE Plume

SOLUTE	DAY	X	Y	DISTANCE TRAVELLED (meters)	AVERAGE SOLUTE VELOCITY (cm/day)	AVERAGE RETARDATION FACTOR
CHLORIDE	6	-3.67	0.98	0.00		
	42	-2.99	4.20	3.29	7.84	1.00
	106	-2.38	8.98	8.10	7.64	1.00
	317	0.71	27.18	26.56	8.38	1.00
	398	3.04	34.56	34.24	8.60	1.00
	476	5.09	44.51	44.40	9.33	1.00
MTBE	6	-3.74	0.85	0.00		
	42	-3.04	4.15	3.37	8.03	0.98
	106	-2.32	9.00	8.27	7.80	0.98
	317	0.63	27.57	27.07	8.54	0.98
	398	3.61	35.47	35.39	8.89	0.97
	476	4.79	42.87	42.88	9.01	1.04
BENZENE	6	-3.77	0.91	0.00		
	42	-2.98	3.95	3.14	7.48	1.05
	106	-2.60	7.94	7.13	6.72	1.14
	317	0.18	24.35	23.77	7.50	1.12
	398	2.42	31.29	31.00	7.79	1.10
	476	3.89	37.54	37.42	7.86	1.19
TOLUENE	6	-3.79	0.83	0.00		
	42	-3.07	3.66	2.92	6.95	1.13
	106	-2.74	7.40	6.65	6.28	1.22
	317	-0.80	20.77	20.16	6.36	1.32
	398	1.60	28.33	28.02	7.04	1.22
	476	2.29	33.35	33.08	6.95	1.34

Table G-1. (continued)

TRANSPORT CALCULATIONS
10% MTBE PLUME

SOLUTE	DAY	X	Y	DISTANCE TRAVELLED (meters)	AVERAGE SOLUTE VELOCITY (cm/day)	AVERAGE RETARDATION FACTOR
ETHYLBENZ	6	-3.80	0.66	0.00		
	42	-3.25	2.99	2.39	5.70	1.37
	106	-2.88	5.92	5.34	5.04	1.52
	317	-1.81	15.41	14.88	4.70	1.78
	398	-0.23	20.44	20.10	5.05	1.70
	476	-0.65	18.65	18.26	3.84	2.43
p-XYLENE	6	-3.81	0.61	0.00		
	42	-3.34	2.72	2.16	5.15	1.52
	106	-2.89	5.64	5.11	4.82	1.58
	317	-1.94	15.21	14.72	4.64	1.80
	398	-0.19	19.73	19.46	4.89	1.76
	476	0.19	20.36	20.15	4.23	2.20
m-XYLENE	6	-3.76	0.61	0.00		
	42	-3.30	2.81	2.25	5.35	1.46
	106	-2.87	6.05	5.51	5.20	1.47
	317	-1.64	18.87	18.38	5.80	1.45
	398	1.70	25.52	25.50	6.41	1.34
o-XYLENE	6	-3.84	0.63	0.00		
	42	-3.31	2.95	2.38	5.67	1.38
	106	-2.94	5.86	5.31	5.01	1.53
	317	-1.80	15.91	15.42	4.86	1.72
	398	0.17	20.86	20.62	5.18	1.66
	476	0.53	22.74	22.54	4.73	1.97

Table G-1. (continued)

TRANSPORT CALCULATIONS
10% MTBE PLUME

SOLUTE	DAY	TIME INTERVAL (days)	DISTANCE INTERVAL (meters)	SOLUTE VELOCITY (cm/day)	RETARDATION FACTOR
CHLORIDE	6				
	42	36	3.29	9.14	1.00
	106	64	4.81	7.52	1.00
	317	211	18.46	8.75	1.00
	398	81	7.68	9.48	1.00
	476	78	10.16	13.02	1.00
MTBE	6				
	42	36	3.37	9.37	0.98
	106	64	4.90	7.66	0.98
	317	211	18.80	8.91	0.98
	398	81	8.32	10.27	0.92
	476	78	7.49	9.60	1.36
BENZENE	6				
	42	36	3.14	8.72	1.05
	106	64	3.99	6.23	1.21
	317	211	16.64	7.89	1.11
	398	81	7.23	8.93	0.98
	476	78	6.42	8.23	1.15
TOLUENE	6				
	42	36	2.92	8.11	1.13
	106	64	3.73	5.83	1.29
	317	211	13.51	6.40	1.17
	398	81	7.86	9.70	0.90
	476	78	5.06	6.49	1.35

Table G-1. (continued)

10% MTBE PLUME

SOLUTE	DAY	TIME INTERVAL (days)	DISTANCE INTERVAL (meters)	SOLUTE VELOCITY (cm/day)	RETARDATION FACTOR
ETHYLBENZ	6				
	42	36	2.39	6.65	1.37
	106	64	2.95	4.60	1.63
	317	211	9.54	4.52	1.66
	398	81	5.22	6.44	1.17
	476	78	1.84	2.35	3.19
p-XYLENE	6				
	42	36	2.16	6.00	1.52
	106	64	2.95	4.61	1.63
	317	211	9.61	4.55	1.65
	398	81	4.74	5.85	1.28
	476	78	0.69	0.89	8.48
m-XYLENE	6				
	42	36	2.25	6.24	1.46
	106	64	3.26	5.10	1.47
	317	211	12.87	6.10	1.23
	398	81	7.12	8.79	0.86
o-XYLENE	6				
	42	36	2.38	6.61	1.38
	106	64	2.93	4.57	1.64
	317	211	10.11	4.79	1.57
	398	81	5.21	6.43	1.17
	476	78	1.91	2.45	3.06

Table G-2. Transport Calculations - 100% PS-6 Plume

TRANSPORT CALCULATIONS
PS-6 PLUME

SOLUTE	DAY	X	Y	DISTANCE TRAVELLED (meters)	AVERAGE SOLUTE VELOCITY (cm/day)	AVERAGE RETARDATION FACTOR
CHLORIDE	6	0.49	1.10	0.00		
	42	1.49	4.40	3.45	8.21	1.00
	106	2.02	9.56	8.60	8.11	1.00
	317	5.29	28.39	27.71	8.74	1.00
	398	7.57	36.18	35.79	8.99	1.00
	476	10.08	45.15	45.08	9.47	1.00
BENZENE	6	0.39	1.00	0.00		
	42	1.37	4.07	3.22	7.67	1.07
	106	1.88	8.95	8.09	7.63	1.06
	317	4.02	23.00	22.30	7.03	1.24
	398	6.73	31.42	31.07	7.81	1.15
	476	7.41	35.11	34.82	7.32	1.29
TOLUENE	6	0.36	0.89	0.00		
	42	1.10	3.67	2.88	6.85	1.20
	106	1.78	8.18	7.43	7.01	1.16
	317	3.58	20.36	19.73	6.23	1.40
	398	6.13	27.48	27.21	6.84	1.32
	476	7.80	34.37	34.30	7.21	1.31

Table G-2. (continued)

TRANSPORT CALCULATIONS
PS-6 PLUME

SOLUTE	DAY	X	Y	DISTANCE TRAVELLED (meters)	AVERAGE SOLUTE VELOCITY (cm/day)	AVERAGE RETARDATION FACTOR
ETHYLBENZ	6	0.25	1.00	0.00		
	42	1.12	3.01	2.19	5.21	1.57
	106	1.38	6.56	5.67	5.35	1.52
	317	2.42	15.03	14.20	4.48	1.95
	398	4.10	21.70	21.05	5.29	1.70
	476	4.61	21.74	21.19	4.45	2.13
p-XYLENE	6	0.24	1.01	0.00		
	42	1.00	2.82	1.96	4.67	1.76
	106	1.33	6.43	5.53	5.22	1.56
	317	2.30	14.28	13.43	4.24	2.06
	398	3.17	16.00	15.27	3.84	2.34
	476	4.00	19.80	19.16	4.03	2.35
m-XYLENE	6	0.30	1.03	0.00		
	42	1.13	3.01	2.15	5.11	1.61
	106	1.36	6.53	5.60	5.28	1.53
	317	3.01	17.66	16.85	5.32	1.64
	398	4.19	19.77	19.14	4.81	1.87
o-XYLENE	6	0.24	0.97	0.00		
	42	1.04	2.91	2.10	5.00	1.64
	106	1.29	6.58	5.71	5.38	1.51
	317	2.51	15.17	14.38	4.54	1.93
	398	3.93	19.40	18.80	4.72	1.90
	476	4.18	21.18	20.59	4.33	2.19

Table G-2. (continued)

TRANSPORT CALCULATIONS
PS-6 PLUME

SOLUTE	DAY	TIME INTERVAL (days)	DISTANCE INTERVAL (meters)	SOLUTE VELOCITY (cm/day)	RETARDATION FACTOR
CHLORIDE	6				
	42	36	3.45	9.58	1.00
	106	64	5.15	8.05	1.00
	317	211	19.11	9.06	1.00
	398	81	8.08	9.97	1.00
	476	78	9.29	11.92	1.00
BENZENE	6				
	42	36	3.22	8.95	1.07
	106	64	4.87	7.60	1.06
	317	211	14.21	6.73	1.35
	398	81	8.78	10.83	0.84
	476	78	3.75	4.81	2.07
TOLUENE	6				
	42	36	2.88	7.99	1.20
	106	64	4.55	7.11	1.13
	317	211	12.31	5.83	1.38
	398	81	7.47	9.23	0.98
	476	78	7.09	9.09	1.00

Table G-2. (continued)

PS-6 PLUME

SOLUTE	DAY	TIME INTERVAL (days)	DISTANCE INTERVAL (meters)	SOLUTE VELOCITY (cm/day)	RETARDATION FACTOR
ETHYLBENZ	6				
	42	36	2.19	6.08	1.57
	106	64	3.48	5.44	1.76
	317	211	8.52	4.04	1.99
	398	81	6.86	8.47	0.95
p-XYLENE	6				
	42	36	1.96	5.45	1.76
	106	64	3.57	5.57	1.72
	317	211	7.90	3.74	2.15
	398	81	1.84	2.28	3.53
	476	78	3.89	4.99	1.61
m-XYLENE	6				
	42	36	2.15	5.96	1.61
	106	64	3.45	5.40	1.77
	317	211	11.25	5.33	1.51
	398	81	2.29	2.83	2.85
o-XYLENE	6				
	42	36	2.10	5.83	1.64
	106	64	3.61	5.64	1.70
	317	211	8.67	4.11	1.96
	398	81	4.42	5.45	1.48
	476	78	1.79	2.30	3.50

Table G-3. Transport Calculations - 85% Methanol Plume

TRANSPORT CALCULATIONS
85% METHANOL PLUME

SOLUTE	DAY	X	Y	DISTANCE TRAVELLED (meters)	AVERAGE SOLUTE VELOCITY (cm/day)	AVERAGE RETARDATION FACTOR
CHLORIDE	6	4.34	1.03	0.00		
	42	5.58	4.72	3.89	9.27	1.00
	106	6.52	10.67	9.88	9.32	1.00
	317	9.13	29.87	29.24	9.22	1.00
	398	12.25	38.78	38.57	9.69	1.00
	476	14.07	44.81	44.85	9.42	1.00
METHANOL	6	4.43	1.19	0.00		
	42	5.57	4.75	3.74	8.90	1.04
	106	6.44	11.00	10.01	9.45	0.99
	317	9.21	29.99	29.19	9.21	1.00
BENZENE	6	4.30	1.01	0.00		
	42	5.54	4.29	3.51	8.35	1.11
	106	6.24	10.18	9.37	8.84	1.05
	317	8.65	26.25	25.61	8.08	1.14
	398	10.51	30.79	30.42	7.64	1.27
	476	11.85	36.54	36.32	7.63	1.23
TOLUENE	6	4.30	0.96	0.00		
	42	5.38	3.74	2.98	7.10	1.31
	106	6.04	8.96	8.19	7.72	1.21
	317	7.98	22.73	22.08	6.96	1.32
	398	9.58	26.44	26.02	6.54	1.48
	476	10.62	30.71	30.41	6.39	1.47

Table G-3. (continued)

TRANSPORT CALCULATIONS
85% METHANOL PLUME

SOLUTE	DAY	X	Y	DISTANCE TRAVELLED (meters)	AVERAGE SOLUTE VELOCITY (cm/day)	AVERAGE RETARDATION FACTOR
ETHYLBENZ	6	4.32	0.80	0.00		
	42	5.13	3.21	2.54	6.05	1.53
	106	5.65	7.49	6.82	6.43	1.45
	317	7.05	14.77	14.23	4.49	2.05
	398	7.75	17.37	16.92	4.25	2.28
	476	8.14	19.34	18.93	3.98	2.37
p-XYLENE	6	4.29	0.75	0.00		
	42	5.11	3.15	2.54	6.04	1.53
	106	5.53	7.08	6.45	6.09	1.53
	317	6.85	14.03	13.52	4.27	2.16
	398	7.80	17.25	16.87	4.24	2.29
	476	8.13	18.66	18.32	3.85	2.45
m-XYLENE	6	4.36	0.73	0.00		
	42	5.12	3.14	2.53	6.02	1.54
	106	5.56	7.10	6.48	6.12	1.52
	317	7.33	16.80	16.34	5.16	1.79
	398	8.26	18.66	18.35	4.61	2.10
o-XYLENE	6	4.28	0.78	0.00		
	42	5.08	3.22	2.57	6.11	1.52
	106	5.69	7.47	6.84	6.45	1.45
	317	7.08	15.45	14.93	4.71	1.96
	398	8.11	18.48	18.11	4.55	2.13
	476	8.59	22.37	22.02	4.63	2.04

Table G-3. (continued)

TRANSPORT CALCULATIONS
85% METHANOL PLUME

SOLUTE	DAY	TIME INTERVAL (days)	DISTANCE INTERVAL (meters)	SOLUTE VELOCITY (cm/day)	RETARDATION FACTOR
CHLORIDE	6				
	42	36	3.89	10.81	1.00
	106	64	5.99	9.36	1.00
	317	211	19.35	9.17	1.00
	398	81	9.33	11.52	1.00
	476	78	6.28	8.05	1.00
METHANOL	6				
	42	36	3.74	10.38	1.04
	106	64	6.28	9.81	0.95
	317	211	19.18	9.09	1.01
BENZENE	6				
	42	36	3.51	9.74	1.11
	106	64	5.87	9.17	1.02
	317	211	16.24	7.70	1.19
	398	81	4.81	5.94	1.54
	476	78	5.90	7.57	1.52
TOLUENE	6				
	42	36	2.98	8.28	1.31
	106	64	5.20	8.13	1.15
	317	211	13.89	6.58	1.42
	398	81	3.94	4.87	1.88
	476	78	4.39	5.63	1.63

Table G-3. (continued)

85% METHANOL PLUME

SOLUTE	DAY	TIME INTERVAL (days)	DISTANCE INTERVAL (meters)	SOLUTE VELOCITY (cm/day)	RETARDATION FACTOR
ETHYLBENZ	6				
	42	36	2.54	7.06	1.53
	106	64	4.28	6.69	1.62
	317	211	7.41	3.51	2.66
	398	81	2.69	3.32	2.82
	476	78	2.01	2.57	3.64
p-XYLENE	6				
	42	36	2.54	7.05	1.53
	106	64	3.91	6.12	1.77
	317	211	7.07	3.35	2.79
	398	81	3.34	4.13	2.27
	476	78	1.45	1.86	5.04
m-XYLENE	6				
	42	36	2.53	7.02	1.54
	106	64	3.96	6.18	1.75
	317	211	9.86	4.67	2.00
	398	81	2.01	2.48	3.78
o-XYLENE	6				
	42	36	2.57	7.13	1.52
	106	64	4.27	6.67	1.62
	317	211	8.10	3.84	2.44
	398	81	3.17	3.92	2.39
	476	78	3.91	5.01	1.87

Table G-4. Estimates of Mass in Solution for each Solute at each Sample Time (grams).

10% MTBE plus 90% PS-6 GASOLINE

Solute	Day 6	Day 42	Day 106	Day 317	Day 398	Day 476
Benzene	19.67	20.81	14.53	8.98	5.85	4.97
Toluene	11.54	14.22	6.75	1.16	0.66	0.20
Ethylbenzene	1.64	1.64	1.19	0.44	0.20	0.05
p-Xylene	1.69	1.95	1.24	0.55	0.20	0.11
m-Xylene	4.45	4.44	1.90	0.21	0.01	0.00
o-Xylene	2.37	2.77	1.90	0.66	0.39	0.20
Total BTEX	41.36	45.83	27.51	12.00	7.31	5.53
Chloride	1410	1130	1150	780	650	1390
MTBE	700	700	670	360	340	600

100% PS-6 GASOLINE

Solute	Day 6	Day 42	Day 106	Day 317	Day 398	Day 476
Benzene	16.22	17.97	13.22	5.04	4.77	2.61
Toluene	10.59	9.30	7.85	1.14	0.12	0.02
Ethylbenzene	1.72	1.45	1.20	0.57	0.08	0.04
p-Xylene	1.66	1.43	1.24	0.56	0.09	0.07
m-Xylene	4.30	4.02	2.28	0.24	0.08	0.00
o-Xylene	2.50	2.40	1.95	0.96	0.21	0.21
Total BTEX	36.99	36.57	27.74	8.51	5.35	2.95
Chloride	1080	1270	970	630	510	1050

Table G-4. (continued)

85% METHANOL plus 15% PS-6 GASOLINE

Solute	Day 6	Day 42	Day 106	Day 317	Day 398	Day 476
Benzene	14.63	17.40	15.89	10.94	8.87	9.24
Toluene	9.17	11.57	8.49	1.79	0.50	0.13
Ethylbenzene	1.31	1.47	0.93	0.66	0.44	0.39
p-Xylene	1.28	1.57	0.91	0.54	0.43	0.30
m-Xylene	3.30	4.09	2.21	0.40	0.09	0.00
o-Xylene	1.87	2.39	1.58	0.92	0.70	0.30
Total BTEX	31.56	38.49	30.01	15.25	11.03	10.36
Chloride	1350	1440	1500	1650	850	1320
Methanol	13560	14440	13440	3590	90	10

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

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Section 1
INTRODUCTION

The laboratory biotransformation experiments described in this report were funded by the American Petroleum Institute (API) and the Ontario University Research Incentive Fund (URIF) as a component of a large-scale study of the chemical fate and impact of oxygenates in groundwater. Other components of the research program include a study of the solubility of BTEX from gasoline-oxygenate mixtures (API, 1991), and a natural gradient tracer injection experiment conducted in a shallow sand aquifer at Canada Forces Base (CFB) Borden (API, 1993).

1.1 Background

The research program was initiated in response to concern that oxygenates might increase the rate of migration and the persistence of the principal monoaromatic constituents - benzene, toluene, ethylbenzene, and xylene isomers (collectively, BTEX) - of gasoline plumes in groundwater. The two oxygenates selected for study were methanol and methyl-tertiary-butyl-ether (MtBE). Both oxygenates are highly soluble in water: MtBE has a solubility of 43,000 mg/L, and methanol is completely miscible. In contrast, BTEX solubilities range from about 200 mg/L (ethylbenzene and the xylenes) to 1800 mg/L (benzene). The oxygenates are therefore likely to be found in groundwater at high concentrations relative to BTEX at a fuel spill site.

Studies have shown that the major factor limiting BTEX persistence in groundwater is biodegradation. The monoaromatics are biodegraded under a wide range of environmental conditions (Gibson and Subramanian, 1984). In aerobic groundwaters, 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 (Major, 1988; Patrick, 1986; Berry-Spark, 1987).

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 (Ludzack and Ettinger, 1960; Harada and Nagashima, 1975), so this compound is unlikely to represent a preferred substrate.

Other inhibitory effects are also possible: for example, high concentrations of either of the oxygenates may be toxic to microbial communities which degrade BTEX. Ingram and Buttke (1984), in their review of the effects of alcohols on microorganisms, 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.

Limited evidence of growth inhibition of benzene degraders by methanol has been found in a laboratory experiment performed at the University of Waterloo. The growth of Pseudomonas bacteria (known benzene degraders) in a basal salts medium spiked with 210 mg/L benzene and varying methanol concentrations was monitored. The Pseudomonas culture grew rapidly in the absence of methanol with benzene as its sole carbon source. Flasks with 16 mg/L, 1,592 mg/L, and 7,960 mg/L of methanol showed bacterial growth patterns which were identical to the control case. Growth of the culture was slightly inhibited in the presence of 15,920 mg/L and 23,880 mg/L methanol. In the case of the highest methanol concentration, 47,760 mg/L, growth was entirely inhibited throughout a ten-day incubation period (B. Butler, pers. comm.).

Results from this study indicate that the toxicity effects of methanol are concentration dependent. Other variables may also play a role. For example, a more diverse microbial population, such as that found in the subsurface, might tolerate higher methanol concentrations than the single strain tested. Conversely, subsurface microbes may be more sensitive to methanol presence because groundwater is deficient in the growth-enhancing nutrients that characterize the mineral salts medium used in the experiment.

The inhibition of BTEX biodegradation by oxygenates -- due to limitation of oxygen availability, to preferred substrate utilization or to toxicity effects -- could lengthen the interval of time that BTEX remains in groundwater before natural remediation occurs. Such an occurrence would be undesirable because of the increased probability that BTEX from gasoline/oxygenate plumes would reach drinking water supplies or environmentally sensitive discharge sites. The oxygenates research program at Waterloo has been designed to explore this potential problem.

1.2 Objectives

The biotransformation experiments were undertaken to aid in the design and interpretation of the natural-gradient tracer test at CFB Borden. The field experiment permitted observation of the numerous processes that simultaneously influence contaminant transport in the subsurface. Supporting laboratory efforts were designed to examine the sorption and biotransformation processes individually, to sort out effects which might be masked in the field. The biotransformation studies had four specific aims:

(1) to assess the ability of the microbial population at the CFB Borden field site to degrade the principal monoaromatic components of gasoline (BTEX) in the presence of MtBE or methanol;

(2) to assess the ability of the Borden microbial population to degrade MtBE and methanol in the presence of dissolved gasoline;

(3) to gain an understanding of the relative rates of biodegradation of BTEX and the oxygenates to aid in the interpretation of field results; and

(4) to examine the role of oxygen availability in BTEX and oxygenate biotransformations in order to elucidate the processes occurring at the center and at the edges of plumes.

1.3 Approach

Microcosms - sealed bottles containing aquifer soil and water - were employed in all of the experiments. These systems provide a batch representation of the biological processes occurring in the subsurface environment. Microcosm studies are useful supplements to field programs because they permit observation and interpretation of biotransformation processes without consideration of the dynamics of solute transport. Through the use of sterile controls, the extent of biotransformation can be isolated from other mass loss processes .

The microcosms were designed to represent the shallow, aerobic portion of the Borden aquifer where the field experiment was conducted. Soil and groundwater from the site were used, and the microcosms remained static throughout the experiments to simulate subsurface conditions. Several authors have reported that substrate concentration can influence rates of biotransformation (Aelion *et al.*, 1989). In order to ensure comparability with the field experiment, initial concentrations of the organics in the microcosms were designed to approximate those in the field injection solutions. Since temperature can affect biotransformation rates, microcosms were incubated in the dark at 10°C, the average temperature of the subsurface in southern Ontario. The site-specific nature of the microcosm design precludes extrapolation of the laboratory results to other sites: however, the combined results of the field and laboratory efforts should yield information that has a more general applicability.

Previous work at the Borden site has shown that transport of oxygen into dissolved gasoline plumes is the rate-controlling factor in BTEX biodegradation when no oxygenates are present (Patrick, 1986). Static microcosms are therefore unlikely to produce accurate estimates of field biodegradation rates. However, they are often useful in identifying the potential for metabolism and the key geochemical constraints on metabolism (Wilson *et al.*, 1985).

Two geochemical constraints on BTEX biodegradation are explored in this study: the presence of oxygenates as potential microbial growth inhibitors or preferred substrates, and the need for oxygen as the electron acceptor. The microcosm approach can provide insights into the relative importance of each of these factors at the CFB Borden field site. In the experiments described below, persistence of the monoaromatics in microcosms containing methanol or MtBE is compared to BTEX persistence in baseline microcosms with no oxygenates. Oxygen availability is also controlled: one set of microcosms is incubated with an unlimited supply of oxygen, while a second set has a limited oxygen supply.

The first experiment represents conditions on the edge of a gasoline plume, where oxygen is available via diffusion from uncontaminated groundwater or admixture due to dispersion. It tests whether methanol or MtBE influences BTEX biodegradation when oxygen availability is not a constraint, and whether the oxygenates themselves biodegrade when oxygen is plentiful.

The second experiment simulates conditions at the center of a gasoline plume, where oxygen is likely to become depleted as the compounds are biotransformed. This experiment permits observation of the changing patterns of BTEX and oxygenate biodegradation as oxygen becomes unavailable for aerobic biotransformation. In particular, it tests whether the microbial

population present in the aerobic zone of the Borden aquifer is capable of using alternative electron acceptors to transform either the oxygenates or the monoaromatics.

Section 2
EXPERIMENTAL DESIGN

Dissolved compounds derived from four fuel types were evaluated in the laboratory experiments:

a) 100% gasoline
b) 85% gasoline and 15% MtBE (v/v)
c) 85% gasoline and 15% methanol (v/v)
d) 15% gasoline and 85% methanol (v/v)

These fuels were contacted with Borden groundwater and diluted to representative field concentrations.

Microcosm experiments were performed simultaneously beginning in the spring of 1988, involving groundwater contacted with the 100% gasoline, 15% MtBE, 15% methanol, and 85% methanol fuels. To ensure constancy of fuel composition, an unleaded gasoline (PS6) was provided by the API for use in the entire research effort.

Biotransformation of dissolved constituents from each of the four fuels was tested under conditions in which oxygen was unlimited (Experiment A), as well as with limited oxygen availability (Experiment B). Experimental designs are detailed below. Materials and methods of microcosm preparation are described in Section 3.

2.1 Experiment A: Unlimited Oxygen Microcosms

The goal of this experiment was to assess BTEX and oxygenate biodegradation in a microcosm environment in which oxygen would not be limiting. Sterile controls were established at the start of the experiment to permit differentiation of biological transformation from other potential mass losses such as sorption to soil grains, leakage from the microcosms, or abiotic transformations.

Sixty-milliliter (mL) glass hypovials were filled with three grams of aquifer material, 20 mLs of gasoline/oxygenate contacted groundwater, leaving approximately 40 mLs of headspace. The soil in each hypovial served as a bacterial inoculum. A diagram of a typical microcosm is shown in Figure 2-1.

Control microcosms were prepared by autoclaving hypovials containing aquifer material on three successive days before use, and by addition of 0.6 mL of a 10% (w/w) solution of sodium azide per microcosm. Sodium azide has been shown to be an effective sterilent in previous studies of the aerobic biotransformation of gasoline constituents (Berry-Spark, 1987).

The target aqueous concentration for BTEX in all of the hypovials was 10-15 mg/L. Target oxygenate levels were: 300 mg/L MtBE (15% MtBE case), 1000 mg/L methanol (15% methanol case) and 7000 mg/L methanol (85% methanol case). These target concentrations approximate those employed in the field experiment. Concentrations were established by saturating Borden groundwater with the gasoline/oxygenate mixtures and diluting to the desired concentrations.

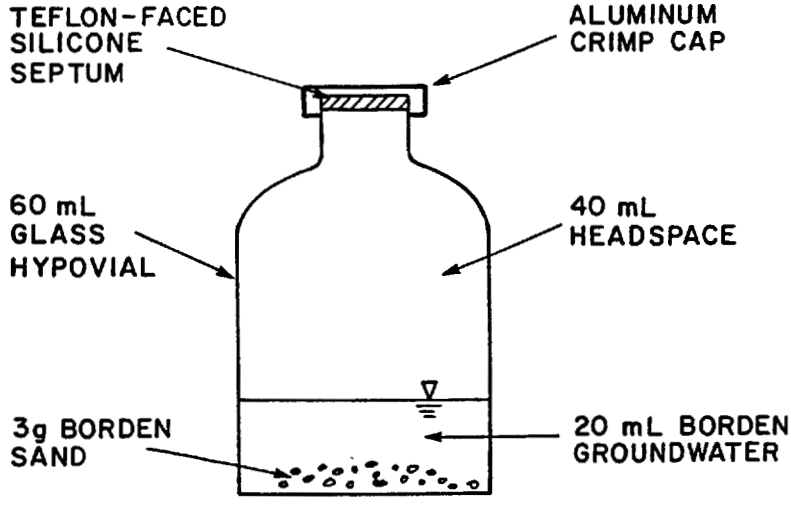

Figure 2-1. Diagram of an Experiment A microcosm.

The large headspace in the hypovials was provided as an oxygen source. Each microcosm contained 0.15 mg of oxygen initially in the water (7.5 mg/L dissolved oxygen) and 10.5 mg of oxygen in the headspace. Although the initial oxygen mass was over 17 times the amount needed to mineralize all of the BTEX in each microcosm, it was insufficient to entirely transform the oxygenates and other gasoline components. Headspace oxygen was monitored in the microcosms throughout the test period to confirm oxygen availability.

Since the systems were not shaken or stirred, there was some concern that oxygen transfer from the headspace to the aquifer material in the microcosms would be slower than the rate of biotransformation, causing the development of anaerobic microsites. Flemming and Trevors (1990) have reported that oxygen consumption by soil microbes is significantly slower in stationary flasks than in shaken flasks. The soil occupied a relatively small volume of each microcosm, so it is unlikely to have represented a significant barrier to oxygen diffusion. It is possible that rates of biotransformation were limited by free water diffusion of oxygen from the air/water interface to the microbes attached to the soil particles. Since all microcosms would be equally affected, this does not compromise the experimental objectives.

Eight sets of triplicate active and control microcosms (192 hypovials) were prepared for each of the four gasoline/oxygenate combinations, permitting eight sampling events. BTEX and oxygenate concentration changes over time were monitored. Concentration changes in active microcosms in excess of changes in sterile microcosms were attributed to biotransformation. Carbon dioxide was monitored to provide a qualitative assessment of the extent of mineralization. Sampling intervals were selected based on the rate of observed mass losses (Table 2-1).

Table 2-1. Sample Times for Unlimited Oxygen Microcosms.

Groundwater contacted by gasoline with:	Days following Start of Incubation							
	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Set 7	Set 8
no oxygenates	1	7	14	21	51	69	114	232
15% MtBE	1	7	14	21	51	69	114	232
15% Methanol	1	7	14	21	51	69	114	232
85% Methanol	1	7	15	26	35	54	103	278

The microcosms were incubated in the dark at 10°C. They were inverted during storage to minimize volatile losses of BTEX and oxygenates. At each sampling session, six microcosms (three active and three sterile controls) were removed from storage, analyzed for the compounds of concern, and discarded.

2.2 Experiment B: Limited Oxygen Microcosms

In this experiment, microcosms were designed to limit the amount of available oxygen in order to assess BTEX and oxygenate biotransformations as conditions became anaerobic. The organic solutes, soil, and groundwater evaluated in this study were identical to those for Experiment A.

Each eighteen-milliliter glass hypovial contained one gram of Borden sand and 18 mL of gasoline/oxygenate contacted groundwater. Control microcosms containing aquifer material were autoclaved on three successive days. Controls for the 100% gasoline, 15% MtBE, and 15% methanol cases received 0.4 mLs of a 7.4% (w/v) mercuric chloride solution. Wolf *et al.* (1989) report that addition of mercuric chloride is a highly effective sterilization procedure. However, unreliable control data from these cases prompted a change to a different bacteriacide for the 85% methanol group, which received 0.2 mLs of a 10% (w/w) sodium azide solution per control microcosm. The reliability of the controls is discussed further in Section 6.

In order to limit oxygen availability, no headspace was left in the hypovials. The oxygen mass in each microcosm was 0.15 mg (7.5 mg/L in groundwater), an amount sufficient to mineralize only 2.4 mg/L of the 10-15 mg/L BTEX present. Dissolved oxygen in the active microcosms was monitored throughout the study to determine when the systems went anaerobic (i.e., oxygen below detection limit of about 0.5 mg/L) and to confirm that no oxygen entered the hypovials.

Eight sets of triplicate active and control microcosms were prepared for each of the four gasoline/oxygenate mixtures. The initial matrix included 192 microcosms. Biotransformation was evaluated by comparing concentrations of the organic solutes over time in active and control microcosms. Sample times for the sets are shown in Table 2-2.

Table 2-2. Sample Times for Limited Oxygen Microcosms

Groundwater contacted by gasoline with:	Days Following Start of Incubation							
	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Set 7	Set 8
no oxygenates	1	7	21	49	120	232	280	420
15% MtBE	1	7	21	49	120	232	280	420
15% Methanol	1	7	21	49	120	232	280	420
85% Methanol*	1	26	48	103	188	278	---	---

*Experiment discontinued after Set 6.

The microcosms were stored at 10°C in BBL GasPak Anaerobic Systems containing disposable hydrogen and carbon dioxide generator envelopes. Each chamber contained one set of microcosms (three active and three controls). Methylene Blue indicator strips were used to monitor the atmosphere in the chambers. Each chamber remained anaerobic until the microcosms were retrieved for analysis.

Section 3

MATERIALS AND METHODS

In microcosm studies which simulate subsurface microbiological conditions, it is essential to make efforts to prevent introduction of nonindigenous microbes, but absolute control is generally unattainable. Standard aseptic technique was used throughout the current study, but it is possible that the microcosms received minor influxes of surface microbes before they were sealed. To ensure that the subsurface microbial population retained an ecological advantage in the systems, soil cores and groundwater were refrigerated before use and the sealed hypovials were incubated at subsurface temperatures. Materials and methods of microcosm preparation and analysis are described below.

3.1 Groundwater and Soil Collection

Soil cores were taken from the site of the field injection experiment at CFB Borden, Ontario (Figure 3-1) on June 9, 1988, three days before the field study began. They were collected from a depth interval of 0.8 m (prevailing water table) to 1.4 m. The collection site was in the aerobic portion of the aquifer, at a location which had not received previous exposure to gasoline. The core material was a finely layered medium-grained sand.

The aquifer material was obtained as aseptically as possible. An aluminum core barrel was sealed with foil, sterilized by successive autoclaving, and transported to the field site. A hole was hand augered to the water table, the foil was removed from one end of the core barrel, and the barrel was driven into the soil. The top end was then capped, causing a vacuum which held the aquifer material in the tube as it was removed. The base was quickly capped as it emerged, and the sealed core was transported to the laboratory and stored at 4°C until use.

Groundwater was collected from a 2-inch PVC well with a slotted screen spanning the water table (see Figure 3-1 for well location). This well was also used to obtain groundwater for the injection solution in the field experiment. Groundwater collection was achieved by using sterile pumping equipment and flushing large volumes of water through sterile glass carboys. Inorganic chemical data obtained from previous studies for groundwater in the upper zone of the Borden aquifer are shown in Table 3-1.

Table 3-1. Chemical Characteristics of the Borden Groundwater (from Mackay *et al.*, 1985 and Patrick, 1986)

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
Total Dissolved solids	380 - 500
Dissolved Organic Carbon	<0.7
Dissolved Oxygen	0 - 8.5
pH	7.3 - 7.9
Temperature(°C)	6 - 12

In general, the shallow Borden groundwater has a low concentration of inorganic nutrients and dissolved organic carbon. Wilson *et al.* (1983) suggest that subsurface bacteria from such settings may be specialized in the capture of metabolizable organic compounds from very dilute solution.

3.2 Preparation of Liquid Media

The Borden groundwater was prepared for dispensing to the microcosms in stages: aeration and sterilization, saturation with dissolved fuel constituents, and dilution to target solute concentrations.

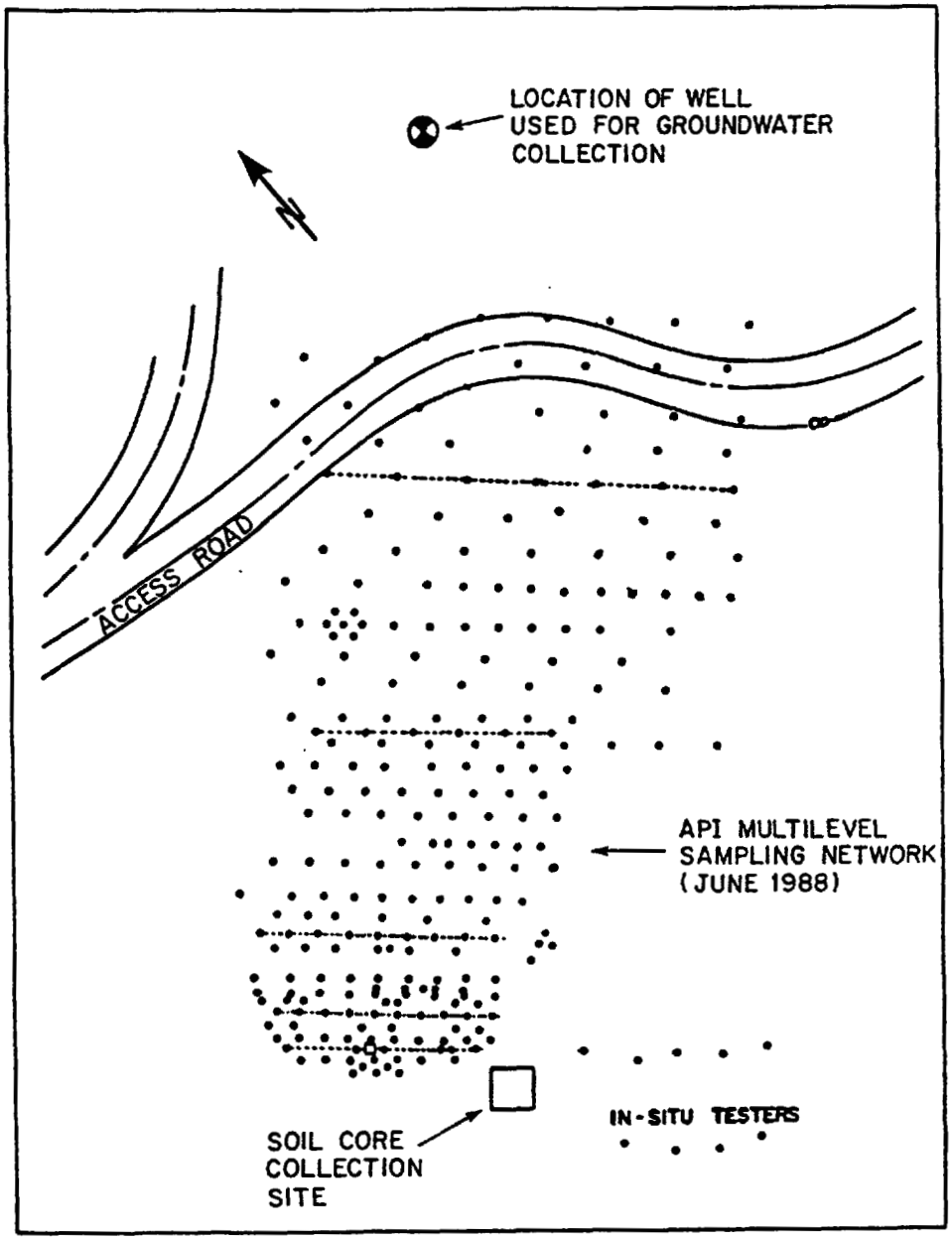

Figure 3-1. Map of the CFB Borden field site showing locations for soil core and groundwater collection. (Scale: 3 mm = 1 m)

Aeration and Sterilization of Groundwater

The groundwater was aerated by purging with sterile air (air passed through a Watman-Gamma-12 filtering system) for six hours, to a dissolved oxygen content of 7.0-7.5 mg/L. A portion of the aerated groundwater was then sterilized in the autoclave.

Creation of Oxygenated Fuels

An API PS-6 Reference unleaded gasoline, characterized chemically by Brookman et. al. (1985), was used. The oxygenates were spectranalysed methanol and analytical grade MtBE. The 85% gasoline/15% MtBE and the 85% gasoline/15% methanol fuels were prepared by mixing the oxygenates with PS-6 gasoline on a volume basis.

Saturation of Groundwater with Fuel Constituents

Aerated, sterile groundwater was contacted with each fuel mixture in a sterile separatory funnel at volume ratios of 10:1 (water:fuel). The funnels were shaken manually for 5 minutes to saturate the water with dissolved organics, and then the water and fuel phases were permitted to separate. This shaking was repeated two more times and the mixtures then equilibrated for 12 hours before use.

Dilution to Target Concentrations

The concentrations of BTEX in gasoline/oxygenate saturated groundwaters were determined by gas chromatography. Dilutions were made with nonsterile groundwater to match target concentrations for BTEX. After dilution, the solutions were stirred for 30 minutes. Table 3-2 lists the BTEX levels in the fuel-saturated groundwater, the target concentrations, and the BTEX levels achieved via dilution.

Table 3-2. Total BTEX Concentrations in Liquid Media (mg/L)

Groundwater contacted by gasoline with:	Fuel Saturated	Dilution Target	Actual* EXPT A	Actual** EXPT B
no oxygenates	115.04	10	8.018	9.259
15% MtBE	97.00	10	7.583	9.422
15% methanol	118.56	10	7.758	9.890
85% methanol	127.37	18	14.514	15.571

* Back calculated from average initial headspace concentration of triplicate control microcosms.
** Average of initial concentrations, back calculated as above, in triplicate control microcosms.

The concentrations of the oxygenates in the dilute solutions are shown in Table 3-3.

For the 15% MtBE and 15% methanol experiments, the oxygenate concentrations in Table 3-3 reflect those present after dilution of the gasoline/oxygenate saturated water. For the 85% methanol experiment, the diluted PS-6 gasoline-contacted groundwater was spiked with methanol to a target concentration of 7000 mg/L.

Table 3-3. Initial Oxygenate Concentrations* (mg/L)

Groundwater contacted by	MtBE		METHANOL	
gasoline with:	EXPT A	EXPT B	EXPT A	EXPT B
no oxygenates	---	---	---	---
15% MtBE	338	310	---	---
15% Methanol	---	---	1039	1028
85% Methanol	---	---	7318	7375

* average of initial concentrations in triplicate control microcosms

3.3 Microcosm Preparation

Asceptic technique was employed throughout the set up of the microcosms. All equipment was sterilized and the microcosms were

prepared under a sterile air flow cabinet to minimize contamination by surface bacteria.

Soil allocation was accomplished by removing the inner portion of the core material and discarding a one centimeter thick annular outer core. Appropriate quantities of soil were weighed into presterilized hypovials which were then resealed with foil. Control microcosms were subsequently autoclaved and chemically killed.

The groundwater containing dissolved fuel constituents was then dispensed via glass/teflon repipets to the hypovials. Immediately after dispensing, each individual microcosm was capped with a teflon-lined silicone septum and aluminum crimp seal.

3.4 Analytical Methods

The microcosms were analyzed for benzene, toluene, ethyl benzene, the three xylene isomers, methanol, MtBE, oxygen and carbon dioxide. The methods for analyzing these compounds are described below. A more detailed description of analytical methods and quality control techniques is provided in Appendix HA.

Monoaromatics (BTEX)

In each of the Experiment A (unlimited oxygen) microcosms, the solutes were distributed between two phases: the groundwater and the air in the headspace. Upon equilibrium the partitioning of the solutes between the two phases can be described by Henry's Law, which governs air-water partitioning in dilute aqueous solutions:

$$P_i = H_{pc}\, C_{iw}$$

where P_i = partial pressure of the component i (atm)
C_{iw} = concentration of i in water (mole/m3)
H_{pc} = Henry's Constant (atm m3/mole)

Volatile compounds like BTEX in closed air:water systems are often analyzed in air and their aqueous concentration calculated via Henry's Law (Garbarini and Lion, 1985). In Experiment A, the monoaromatics were analyzed in the headspace, and data were converted to aqueous concentrations using Henry's Law. The method of conversion is detailed in Appendix HB. Conversions were made based on the assumption that the high concentrations of the oxygenates in the aqueous phase would not interfere with the air-water partitioning of BTEX. Poulsen *et al.* (1991) found that MtBE had negligible effect on solubility of the monoaromatics, and that cosolubility effects of methanol became significant only at concentrations above 20,000 mg/L. At the concentrations tested in this study, the oxygenates are unlikely to have exerted a substantial effect on the Henry's Law constants for BTEX since they have little influence on solubility. Implications of this assumption for data interpretation are discussed in Section 4.

The headspace analysis of the monoaromatics proceeded as follows. Microcosms were removed from the 10°C incubator, shaken vigorously, and placed in a room-temperature water bath for one hour. The shaking procedure was intended to promote equilibrium air/water partitioning. The water bath temperature was recorded to permit use of appropriate Henry's Law constants in conversion to aqueous concentrations. The microcosm headspace was sampled by piercing the septum with the tip of a gastight syringe, flushing three times, pulling the plunger out slowly for a fourth time, and holding it for thirty seconds. The gas sample was then injected into a sampling loop and loaded onto a Shimadzu gas chromatograph (GC) with a flame ionization detector. The GC column and operating conditions were similar to those used for Experiment B and are described in Appendix HA.

The method detection limit for the monoaromatics in the air phase using this technique is 1-2 µg/L. The detection limit for the aqueous phase varied according to the temperature at which the

microcosms were analyzed. The temperature of the waterbath ranged from 20°C to 27°C. The headspace detection limit of 1-2 µg/L corresponds to an aqueous detection limit of 4-8 µg/L for benzene at 25°C based on a Henry's Law conversion.

The Experiment B (limited oxygen) microcosms had no headspace: they were entirely filled with water. The monoaromatics were therefore measured in the water phase. BTEX were analyzed using solvent extraction followed by gas chromatography. The technique is described in detail by Patrick *et al.* (1985) and summarized in Appendix HA. The detection limit for the monoaromatics using this method is 1-2 µg/L.

Methanol and MtBE

Methanol and MtBE in both experiments were analyzed by direct aqueous injection into a gas chromatograph. The method is described in Appendix HA. The detection limit is about 100 µg/L for methanol and about 250 µg/L for MtBE.

Oxygen and Carbon Dioxide

The oxygen and carbon dioxide content of the unlimited oxygen microcosms was determined by gaseous headspace analysis on a Fisher-Hamilton Gas Partitioner with a 1.0 mL sampling loop.

Dissolved oxygen measurements for the limited oxygen microcosms were made using the azide-modified Winkler technique. The method is described in detail by APHA *et al.* (1985). Reagents were added to the 18 mL microcosms with the caps in place (with a syringe tip vent to avoid pressure buildup) using a 1 mL plastic syringe in order to reduce the chances of contamination by atmospheric oxygen. A 0.1 mL aliquot of manganese (II) sulphate solution and 0.1 mL alkali-iodide-azide solution were added to each microcosm. The hypovial was then shaken 20 times and the flocculent permitted to settle. A 1 mL aliquot of phosphoric acid was added, and the acidified water was transferred to an

erlenmeyer flask and titrated using a standardized 0.00025 N sodium thiosulphate solution. Starch was added as an endpoint indicator. The detection limit for this method is 0.2 - 0.7 mg/L.

Section 4
INTERPRETATION OF MICROCOSM DATA

The microcosm approach constitutes a batch determination of the ability of a microbial population to degrade a compound within a given timeframe and under a specific set of environmental conditions. Two parameters are established from microcosm studies: the acclimation period prior to any observable biodegradation of a compound, and the subsequent rate of biotransformation. Together these factors describe the persistence of the compound in the microcosm.

There are several mechanisms which may account for the acclimation period commonly observed before the onset of detectable biodegradation. It may represent the time needed for enzyme induction or genetic alterations. Time may be required before a degrader population becomes sufficiently large to produce a measurable biodegradation rate. Environmental factors, such as insufficient nutrients or preferential substrate utilization, may also play a role. Time may also be needed for the degraders to acclimate to toxins or inhibitors in their environment (Wiggins *et al.*, 1987). In some cases, microbial communities have been shown to be preadapted to some compounds, and no acclimation period is observed (Aelion *et al.*, 1987).

Many of the factors which have potential to cause or prolong an acclimation period can also affect rates of biotransformation. In this study, persistence of the organic solutes is influenced by the presence of the oxygenates (potential toxins or preferred substrates) and the availability of a key electron acceptor (oxygen). The absolute persistence of the solutes in the microcosms is unlikely to match their persistence in the field: however, the relative persistence of the solutes under different chemical conditions can provide clues to their field behavior. Changes in solute persistence which are of a magnitude that will

affect subsurface travel distances are of greatest interest. Groundwater at the CFB Borden field site flows at about 9 cm/day, so factors which increase (or decrease) persistence on the order of months (rather than days or weeks) can be considered significant.

This section outlines the methods of data interpretation used to describe the persistence of the compounds in the microcosms, and identifies potential sources of error and data variability.

4.1 Data Variability and Sources of Error

Caution must be exercised in interpreting batch microcosm data. Although the hypovials for each set are incubated in the same location at the same temperature, each individual microcosm is essentially a separate experiment, and biotransformation rates may differ for microcosms of identical design. Thus, when replicate microcosms are analyzed at each sampling period, widely differing mass losses may be observed.

The variation in biotransformation rates occurs in part because the distribution of subsurface microbes is not uniform, and the soil in a laboratory microcosm will not necessarily include a representative sample of the microbial community that a contaminant plume would encounter as it migrates in the subsurface. Studies of the distribution of microbes in the groundwater environment are still in their early stages, so there is no generally recognized elementary volume of an aquifer that can be considered representative (S. Hipkin, pers. comm.).

For these experiments, triplicate microcosms were employed, both for the sterile controls and for the active sets. The mean, standard deviation, and coefficient of variation were calculated for the triplicates of Experiment A (unlimited oxygen), and these data are tabulated in Appendix HC. The average coefficient of variation for total BTEX in Experiment A is given in Table 4-1.

In general, the variation is small for the sterile controls and large for the active microcosms in which solutes are undergoing biotransformation. Note that for the 85% methanol case, in which little biotransformation of BTEX was observed, the variability for triplicates from the active microcosms is similar to that for the sterile controls.

Table 4-1. Average Coefficients of Variation for BTEX Measured in Triplicate Microcosms of Experiment A.

Groundwater contacted by gasoline with:	Active Microcosms	Control Microcosms
no oxygenates	32%	5%
15% MtBE	52%	8%
15% methanol	29%	9%
85% methanol	5%	4%

Variations in the control data result from nonbiological factors such as differences in initial concentration due to volatile losses during microcosm preparation or to analytical imprecision. Theoretically, these should not show any trend with time. Variability in biological uptake of the substrates for individual microcosm sets can be determined by subtracting the variation in the control data from the variation in the data from biologically active microcosms. The pattern that emerges is one of increasing variability with increasing time for a biodegrading compound, until the detection limit is reached as illustrated in Figure 4-1 for benzene in active and control microcosms from the no oxygenates case of Experiment A. The large variability in the data from the active microcosms suggests that considerable inaccuracies in determining the rate of mass loss of a solute with time will exist.

Sampling frequency may also contribute to poor definition of mass loss. Sampling frequency is established at the start of the experiment and the researcher uses best judgement in choosing appropriate sampling times. However, if sampling episodes are

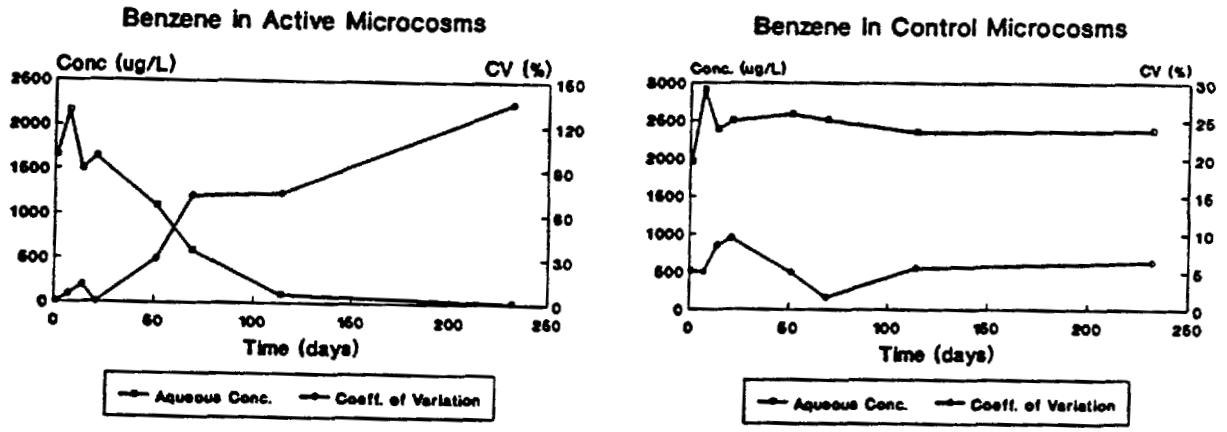

Figure 4-1. Microcosm data variability for a biodegrading compound.

too infrequent during periods of critical mass loss, rate estimates may be inaccurate. Inappropriate sampling frequency may also contribute to difficulties in determining where the acclimation period ends and biotransformation begins.

Owing to these constraints, batch microcosm experiments rarely produce accurate estimates of biotransformation rates. In this study, an assessment of rates of biotransformation in the microcosms was made to facilitate comparison of biotransformation under different conditions. Rates and rate orders reported here are thought meaningful only in a relative sense.

4.2 Assessment of Solute Persistence

Decreases in mass due to biotransformation were calculated by normalizing the aqueous concentrations in the biologically active microcosms to those of the sterile controls. This was accomplished by dividing the active and control data for each sample date by the average control from that date. This

normalization tends to obscure temporal variation occurring in both active and control microcosms caused, for example, by analytical bias for a particular sampling time. In particular, water-air partitioning may vary between sampling times due to changes in ambient temperature. Normalizing data removes any trends due to this type of problem. Since the oxygenate concentrations remained rather constant in all experiments, no bias has been introduced into the normalized data due to variation of water-air partitioning because of variable oxygenate concentration. Figure 4-2 illustrates the normalization process.

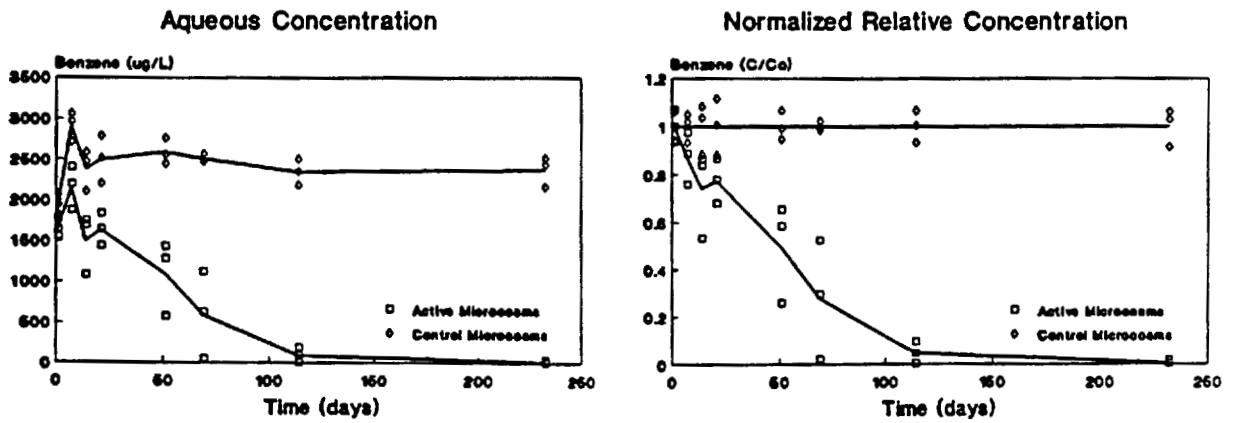

Figure 4-2. Illustration of procedure for normalizing to control data.

Common among the oxygen unlimited experiments is rapid initial biotransformation with tailing at late times. Tailing was observed by Patrick *et al.* (1986) in both the field and laboratory. This phenomenon has been explained as a threshold concentration effect: when the concentration of an organic compound drops below a minimum level, the rate of energy extraction from substrate consumption is not sufficient to maintain cell growth (Alexander, 1985). The tailing may also result from a nutrient limitation.

The rate of decrease in organic solute concentration observed in the active microcosms of this study can be described by zero order kinetic models, by first order kinetic models or by hybrid (zero order initially, then first order). Simkins and Alexander (1984) summarized the implications of such rate orders. A straight line can be fit to the steep, early portion of the curve (zero order), or a line can be fit to a semilog plot of the entire data set (first order). Some of the curves exhibit no tailing: these can be explained by a zero order kinetic process or by a first order process in which the "tail" is below the detection limit for the solute.

The primary need in this study was to compare mass loss behavior under different conditions, not to determine the kinetics of that process (an aim not effectively met with microcosm experiments, as mentioned above). Therefore, whatever model provided the best visual fit to microcosm mass loss curves was used to describe that curve. Generally, zero order rates of biotransformation were calculated for all of the experiments and first order rates were determined only where warranted by the shape of the curves. All rates were calculated for post-acclimation data.

Biotransformation was considered to have occurred if mass loss in the active microcosms was greater than one standard deviation of the controls. This criterion was helpful in distinguishing mass losses for solutes with a long acclimation period and a slow rate of biotransformation.

Section 5
RESULTS OF EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

This experiment examined the aerobic biotransformation of dissolved constituents in groundwater contacted by four fuel blends: PS-6 gasoline with no oxygenates, with 15% MtBE, with 15% methanol, and with 85% methanol. Oxygen availability was unlimited. Sterile control data, oxygen usage and carbon dioxide production, and the persistence of the organic solutes in the microcosms are described below. Experimental data are tabulated in Appendix HC.

5.1 Sterile Control Data

Mean concentrations of the organic solutes in the sterile controls remained within a few percent of the initial level throughout incubation periods ranging from 232 to 278 days. A gradual decline in mean solute concentration was observed over time for some of the sets. The decrease may have resulted from slow diffusion of the compounds through the hypovial septa. The coefficients of variation for BTEX concentrations in triplicate microcosms ranged from 4% to 9% (Table 4-1), with no trend in variability with time.

5.2 Oxygen Availability and Carbon Dioxide Production

Graphs of percent oxygen and percent carbon dioxide in the headspace of the active and control microcosms are presented in Appendix HC. The levels of oxygen and carbon dioxide remained at atmospheric concentrations (21% oxygen, <0.1% carbon dioxide) in the control microcosms over time. In the active microcosms of all four cases, oxygen remained plentiful throughout the incubation period. Mean oxygen levels dropped to only 2%-3% less than the controls by the end of each experiment. Carbon dioxide production in the active microcosms remained stable for one week, then increased through Day 120 in all four cases. The well-buffered Borden groundwater-sand system would not permit

significant pH declines due to this production of CO_2. As discussed below, the first 120 days corresponded to the period of greatest BTEX mass loss in the active microcosms.

5.3 Solute Persistence

This section describes the patterns of biotransformation for the oxygenates and the monoaromatic compounds. Figures 5-1 through 5-7 are plots of aqueous concentration vs. time for organic solutes in active and control microcosms. In the case of the monoaromatics, which were analyzed in the air phase, the data represent aqueous concentrations calculated using Henry's constants and normalized to 25°C.

PS-6 Gasoline with No Oxygenates. This set of microcosms serves as a baseline for comparison with those sets which were spiked with oxygenates. Table 5-1 shows initial concentrations of BTEX and calculated rates of biotransformation. Changes in BTEX concentration over time are depicted in Figure 5-1.

Table 5-1. Summary of Results: Unlimited Oxygen Microcosms of PS-6 Gasoline with No Oxygenates (incubation period of 232 days)

Compound	Initial Conc. (µg/L)	Acclimation Period (days)	Zero Order Rate (µg/L/day)	First Order Rate (d^{-1})
Benzene	1903	<7	15	0.024
Toluene	839	<7	15	0.037
Ethylbenzene	92	<7	2	0.031
p-Xylene	85	<7	2	0.025
m-Xylene	216	<7	8	0.038
o-xylene	168	<7	2	0.030

Acclimation periods preceeding the onset of biodegradation were less than a week for all of the monoaromatics. The Day 1 concentrations of BTEX were lower in the active microcosms than in the control microcosms, indicating that some biotransformation may have occurred between initial set up and the Day 1 analysis.

Toluene, ethyl benzene, and the xylenes were removed to below detection within 114 days in the biologically active microcosms. Benzene was almost entirely removed as well: on average, only 10 µg/L remained in the aqueous phase by Day 232.

As shown in Table 5-1, the zero order biotransformation rates for benzene, toluene, and m-xylene were higher than those for p-xylene, o-xylene, and ethyl benzene. The first order rates were highest for toluene and m-xylene and lowest for benzene, although in general the rates were very similar for all of the monoaromatics. The difference in relative biotransformation rate for benzene for the two kinetic models simply reflects the shape of the mass loss curve: although initial rates of loss were fairly rapid (resulting in a high zero order rate determination), the tailing effect is pronounced (low first order rate).

PS-6 Gasoline with 15% MtBE

Results of this experiment are summarized in Table 5-2. A graph illustrating MtBE persistence in the microcosms is shown in Figure 5-2, and BTEX persistence is illustrated in Figure 5-3.

Table 5-2. Summary of Results: Unlimited Oxygen Microcosms of PS-6 Gasoline with 15% MtBE (incubation period of 232 days)

Compound	Initial Conc. (µg/L)	Acclimation Period (days)	Zero Order Rate (µg/L/day)	First Order Rate (d^{-1})
Benzene	2491	<7	20	0.021
Toluene	1261	<7	21	0.047
Ethylbenzene	139	<7	2	0.088
p-Xylene	133	<7	4	0.044
m-Xylene	361	<7	15	0.058
o-Xylene	248	<7	7	0.047
MtBE	338,000	>232	--	--

No biodegradation of MtBE was observed during the 232 days of incubation. Sufficient oxygen was available in the microcosms to

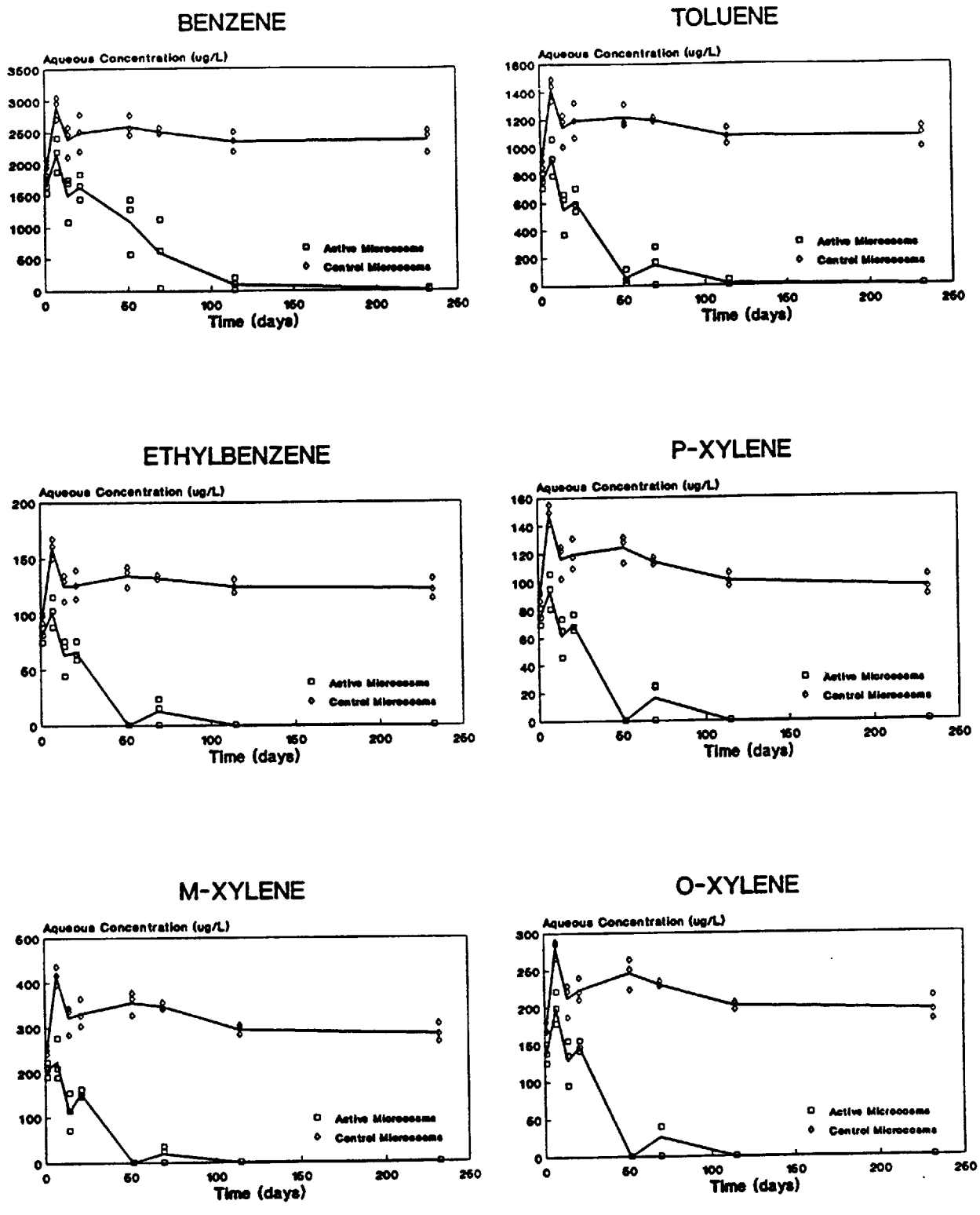

Figure 5-1. BTEX persistence in unlimited oxygen microcosms; PS-6 gasoline with no oxygenates.

permit mineralization of 193 mg/L of MtBE, or about 57% of the initial concentration. However, smaller losses would have been difficult to detect. The average coefficient of variation for the control data was 2%, or about 6760 µg/L. Biotransformation of this quantity (or less) would not be detectable.

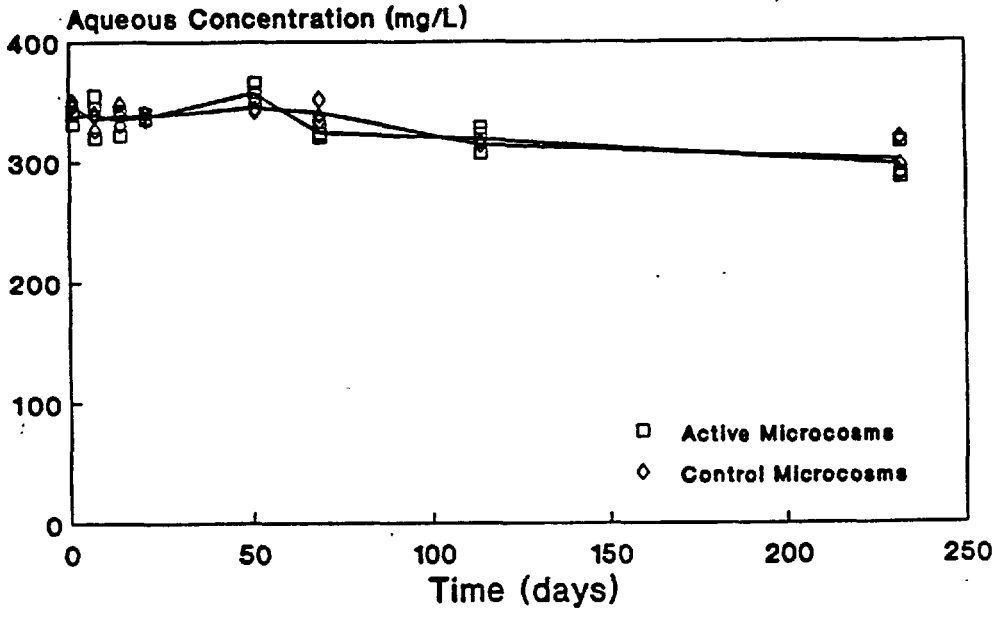

Figure 5-2. MtBE persistence in unlimited oxygen microcosms; PS-6 gasoline with 15% MtBE.

The presence of the MtBE had no significant effect on the duration of the acclimation periods or on the mass removal rates of the monoaromatic compounds: they were similar to those observed in the baseline case. Minor deviations from the baseline case included less tailing in the biodegradation curves and slightly higher first order biotransformation rates for toluene, ethyl benzene, and the xylenes.

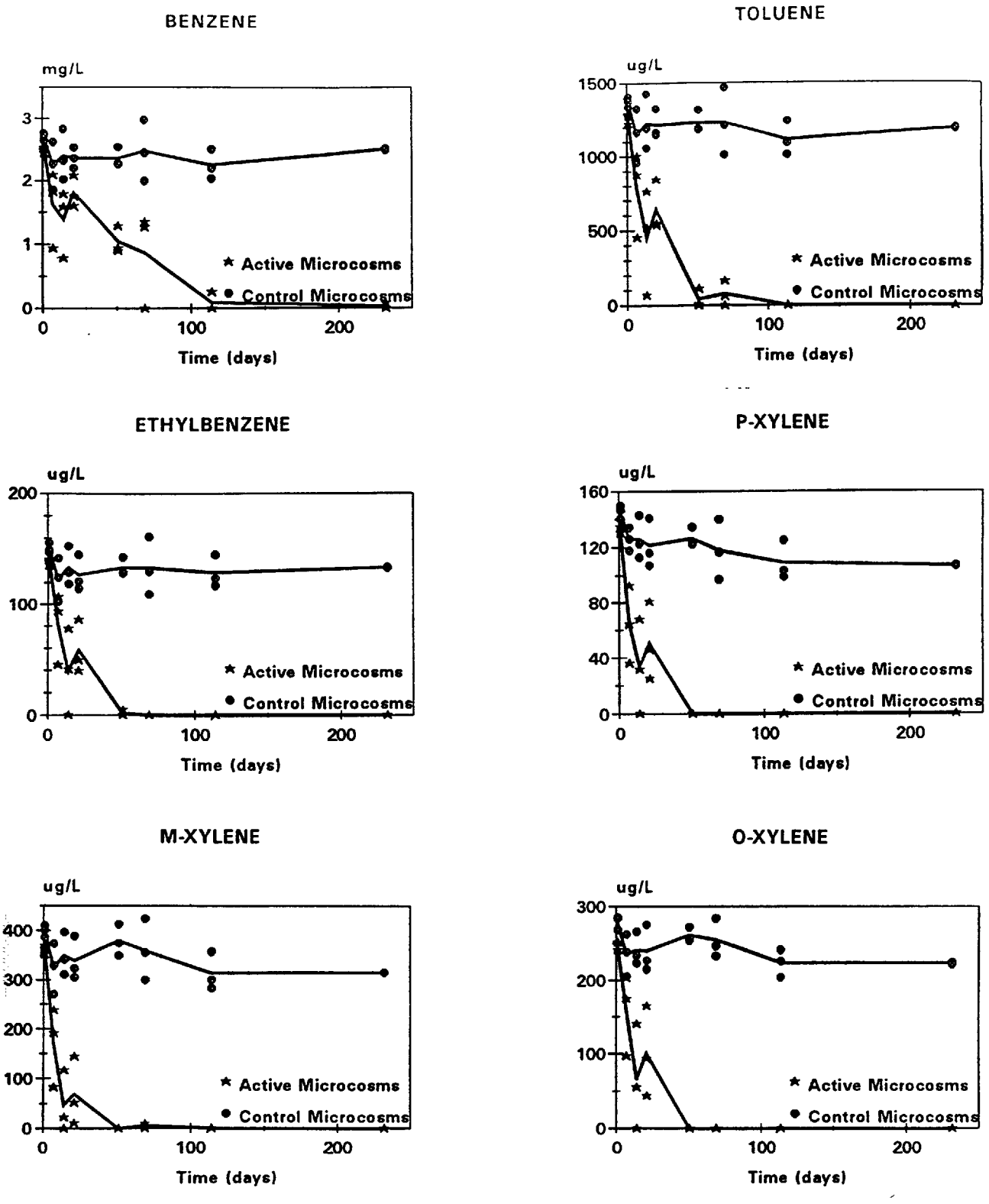

Figure 5-3. BTEX persistence in unlimited oxygen microcosms; PS-6 gasoline with 15% MtBE.

PS-6 Gasoline with 15% Methanol. A summary of results from this experiment is provided in Table 5-3. Figure 5-4 illustrates methanol persistence in the microcosms, and Figure 5-5 depicts BTEX mass loss curves.

Table 5-3. Summary of Results: Unlimited Oxygen Microcosms of PS-6 Gasoline with 15% Methanol (incubation period of 232 days)

Compound	Initial Conc. (µg/L)	Acclimation Period (days)	Zero Order Rate (µg/L/day)	First Order Rate (d^{-1})
Benzene	2538	21	13*	0.006*
Toluene	1242	7	60	0.088
Ethylbenzene	134	7	17	0.077
p-Xylene	143	<7	11	0.048
m-Xylene	290	<7	22	0.076
o-Xylene	228	<7	18	0.048
Methanol	1,039,000	>114	--	--

* calculated for Day 21 to Day 114 interval

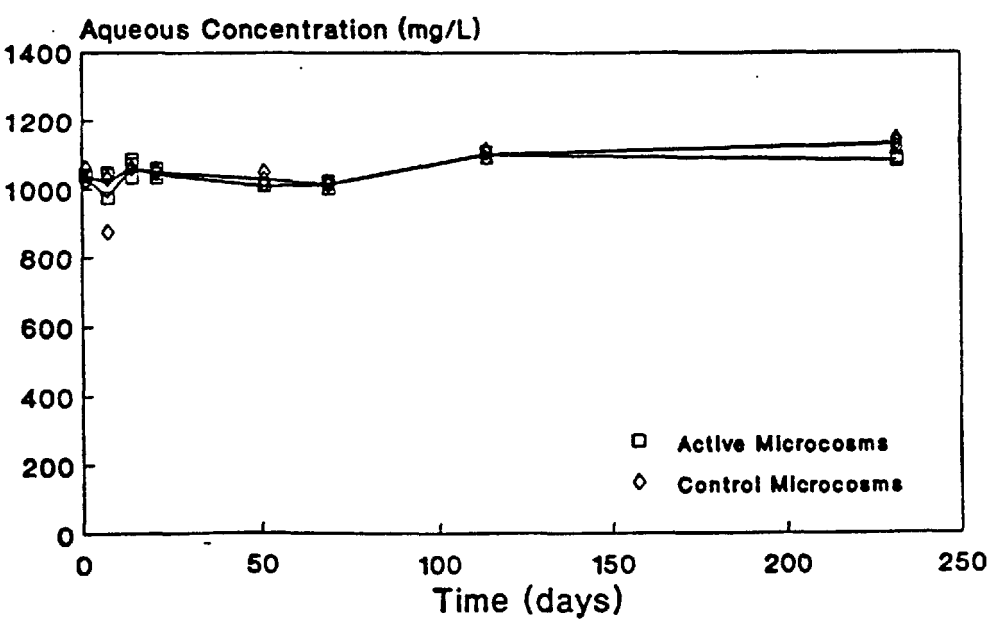

Figure 5-4. Methanol persistence in oxygen unlimited microcosms of PS-6 gasoline with 15% methanol.

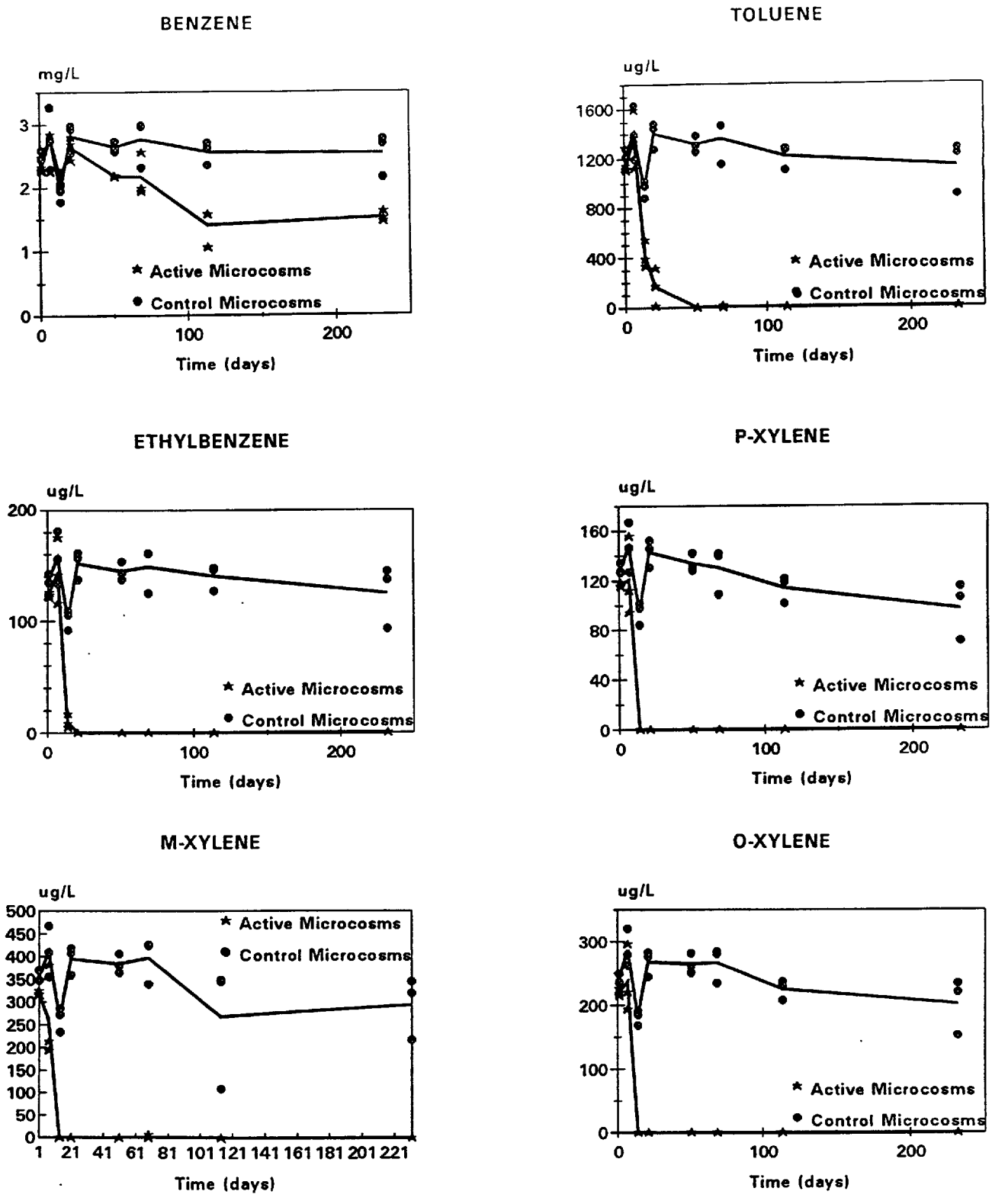

Figure 5-5. BTEX persistence in unlimited oxygen microcosms; PS-6 gasoline with 15% methanol.

No methanol degradation was apparent, but again small concentration declines would not be detected. The average coefficient of variation for the controls was 1%, or 10,390 µg/L. Biotransformation of this significant quantity would not be detected. Sufficient oxygen was available in the microcosms to mineralize 375 mg/L of methanol, about 36% of the initial methanol mass, so oxygen was not likely limiting methanol biodegradation.

The acclimation period for benzene increased to about three weeks, a significant increase relative to the baseline case with no oxygenates. The rate of biotransformation for benzene after Day 21 was slower than in the baseline case, and biotransformation appears to have ceased between Day 114 and Day 232. No acclimation periods were observed for the xylenes, but toluene and ethylbenzene acclimation periods increased to seven days. Biotransformation rates of toluene, ethyl benzene, and the xylenes were slightly enhanced relative to the baseline case. All five unsubstituted monoaromatics were below detection by Day 49. The period of rapid mass loss of these compounds corresponded to a period in which no biotransformation of methanol was observed.

PS-6 Gasoline with 85% Methanol

Table 5-4 summarizes results from this experiment. This set is not directly comparable with the baseline case because the initial concentration of BTEX was slightly higher (15 mg/L instead of 10 mg/L). Figure 5-6 shows the persistence of methanol in the microcosms and Figure 5-7 depicts BTEX mass loss curves.

No methanol biodegradation was detected during the first 103 days of this experiment, but there was a loss of mass between Days 103 and 278 in at least one biologically active microcosm. Loses of about 60 mg/L would have been within the average coefficient of

Table 5-4. Summary of Results: Unlimited Oxygen Microcosms of PS-6 Gasoline with 85% Methanol (incubation period: 278 days)

Compound	Initial Conc. (µg/L)	Acclimation Period (days)	Zero Order Rate (µg/L/day)	First Order Rate (d^{-1})
Benzene	4528	>278	--	--
Toluene	2846	>103	--	--
Ethylbenzene	359	54	1	0.003
p-Xylene	319	>103	--	--
m-Xylene	872	>103	--	--
o-Xylene	544	>103	--	--
Methanol	7,318,000	>103	--	--

variation for methanol in the control microcosms. The apparent mass loss in at least one active microcosm (about 2000 mg/L) greatly exceeded this. Oxygen sufficient to permit aerobic mineralization of only 375 mg/L of methanol was present, so, if biotransformation had occurred, much of it would be anaerobic biotransformation.

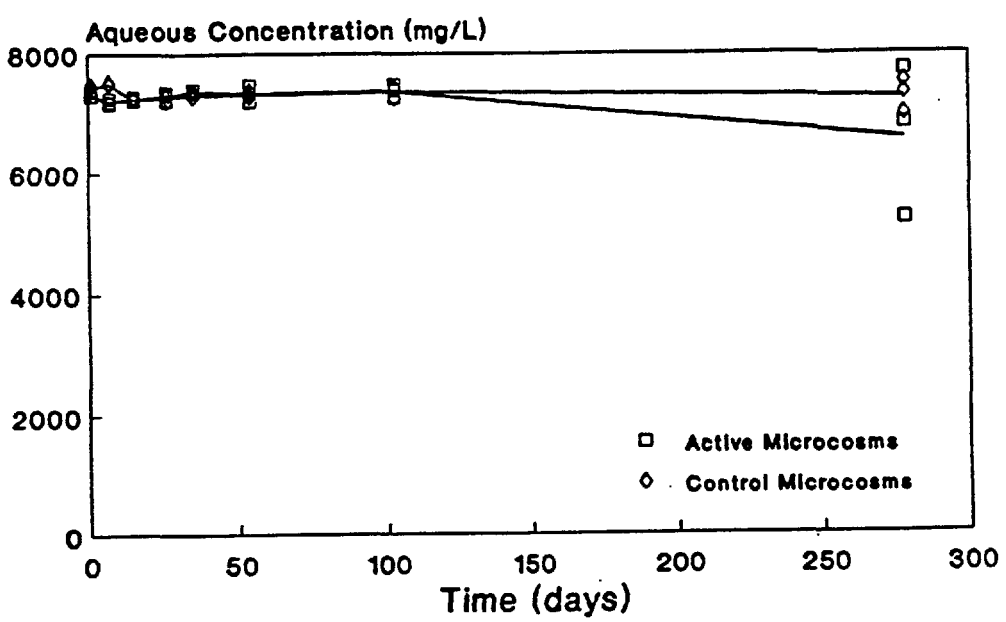

Figure 5-6. Methanol persistence in unlimited oxygen microcosms of PS-6 gasoline with 85% methanol.

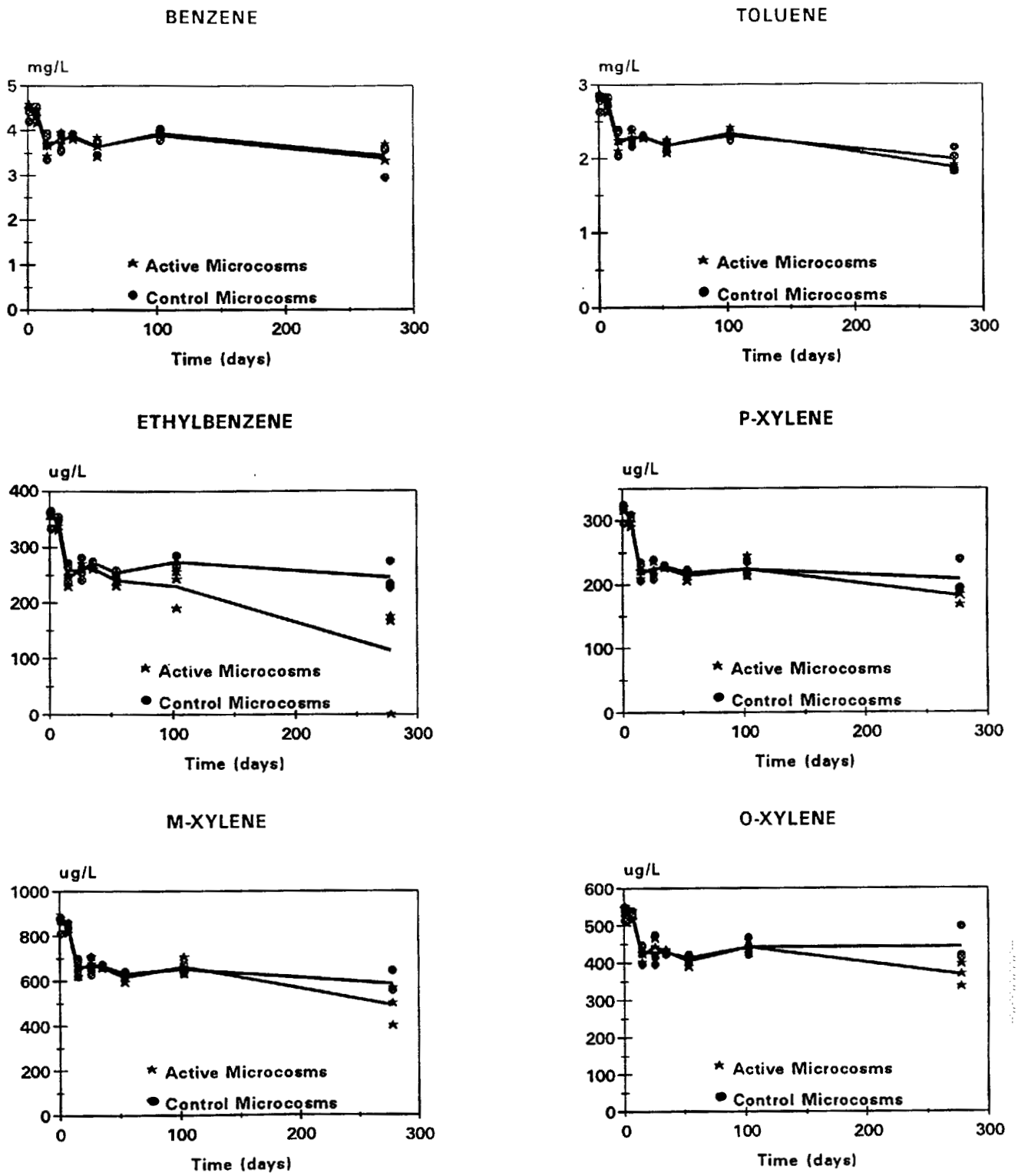

Figure 5-7. BTEX persistence in unlimited oxygen microcosms of PS-6 gasoline with 85% methanol.

The high concentration of methanol present in this set of microcosms, about 7320 mg/l, appears to have entirely prevented benzene degradation. Transformation of toluene and all three xylene isomers was also severely curtailed. No degradation of these compounds was observed until after Day 103. Between Day 103 and Day 278, less than 15% of the mass of these compounds was lost. Ethyl benzene degradation was least affected by the presence of the methanol: losses began after Day 54, and over 50% of the mass had been removed by day 278. The rate of ethylbenzene biotransformation was significantly slower than in the baseline case with no oxygenates.

Section 6
RESULTS OF EXPERIMENT B: LIMITED OXYGEN MICROCOSMS

Experiment B examined the biodegradation of BTEX and oxygenates in gasoline-contacted groundwater under initially aerobic and then anaerobic conditions. The four gasoline/oxygenate blends used in Experiment A were also tested in this study. Experimental results are described below, and data are tabulated in Appendix HD.

6.1 Sterile Control Data

Control data for these experiments were highly variable. In the no-oxygenates, 15% MtBE, and 15% methanol cases, there appeared to be substantial mass losses of BTEX for one or two microcosms in each triplicate set after the first week of incubation. The apparent losses ranged from 20%-30% to nearly 100%, and showed no obvious trend with time. Each sampling period also yielded at least one control microcosm with BTEX concentrations remaining within a few percent of the initial levels. The MtBE control data were similar to the BTEX data, while the methanol controls showed very little variability.

There are several possible explanations for the unusual control data. The controls differed from the active microcosms in that they contained autoclaved soil and mercuric chloride as a bacteriacide. It is possible that abiotic reactions involving the sterilent and the soil may have led to gas production in the control microcosms. While loss of BTEX into any headspace so created would not be significant, based on the estimation method suggested by Pankow (1986), generation of gas pressure could have caused leakage around the septa of some hypovials.

Direct oxidation of organics by mercuric chloride is possible, but is unlikely to be so sporadic. An alternative explanation is that some controls became microbially active. This possibility

is relatively unlikely. In previous studies using mercuric chloride with Borden groundwater and soil, gas production and BTEX losses were also observed in anaerobic control microcosms, and sterility was confirmed via microbial assay (Berry-Spark, 1987). Furthermore, if the controls became biologically active, patterns of BTEX losses would be expected to be similar for active and control microcosms, yet the two appeared unrelated.

A further possibility is that the contacted groundwater may have been dispensed incorrectly to some of the control microcosms. BTEX could have volatilized at some early stage of microcosm preparation. The initial BTEX concentration would then be low in some of the hypovials, and the low levels would appear as mass losses when the microcosms were later analyzed.

The 85% methanol microcosms were prepared at a later date, and received sodium azide instead of mercuric chloride as a bacteriacide. BTEX control data showed a gradual decline with time and a few control microcosms had substantial losses (50-70%) at the final sampling event on Day 278. Sodium azide is considered a less effective sterilent than mercuric chloride under anaerobic conditions, so it is possible that control microcosms became microbially active near the end of the experiment: microbial activity may even have been enhanced by the presence of the azide, which has been shown to affect pH (Wolf, 1989). Concentrations of methanol in the controls showed no change with time.

Thus, we consider it unlikely that biotransformation caused significant mass loss in controls. the mass loss by this unknown mechanism in the controls is not expected to have influenced the active microcosms. Therefore, selective use of the BTEX and MtBE control data was necessary to interpret the data from the active microcosms. Only those control microcosms in which solute levels were consistently high over time were considered reliable. This

renders the interpretations of this section somewhat speculative. For future work with limited oxygen systems, alternative sterilents should be sought.

6.2 Oxygen Availability

In general, oxygen was consumed rapidly in the microcosms (Figure 6-1). In the case of PS-6 gasoline with no additives, oxygen was entirely depleted after one week. In the 15% MtBE and 15% methanol cases, oxygen was absent by the third week. In the 85% methanol case, oxygen was at the detection limit by Day 26 and below detection by the seventh week.

6.3 Solute Persistence

This section describes the biotransformation of BTEX and the oxygenates in the four cases tested. For the monoaromatics, mass

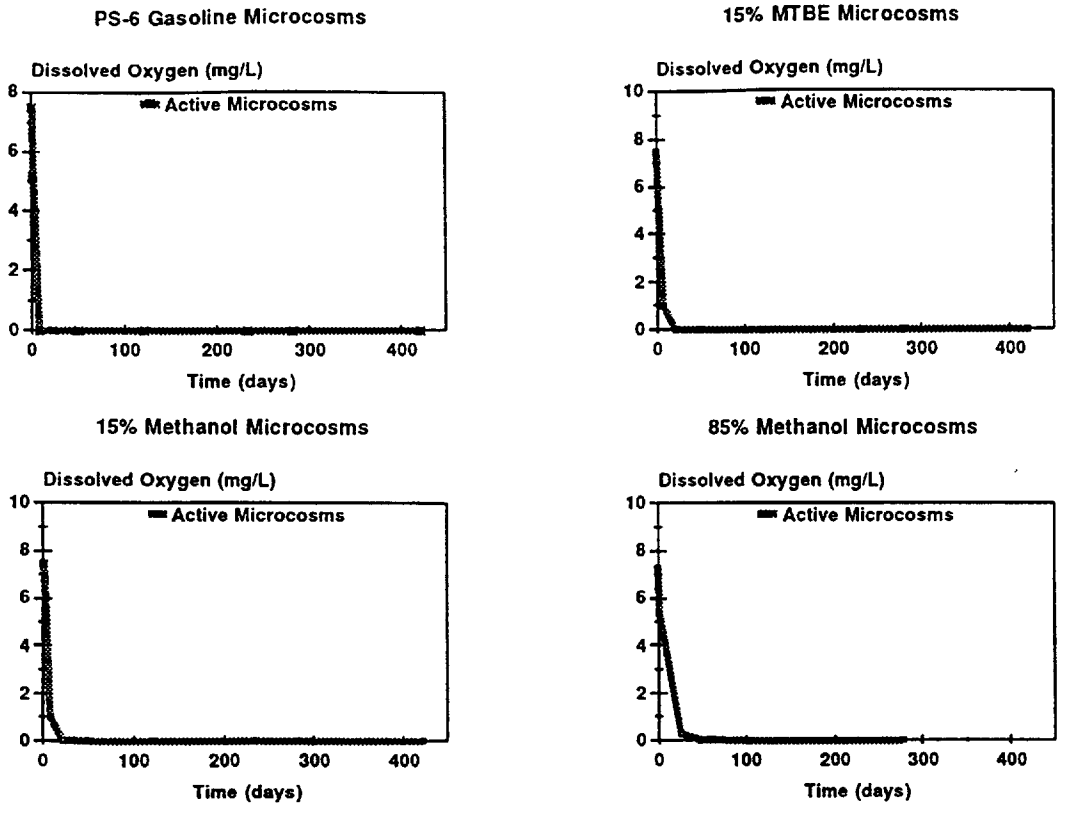

Figure 6-1. Dissolved oxygen levels in active microcosms of Experiment B.

reductions due to aerobic biotransformation were determined by calculating the mean of the normalized data for the aerobic period and subtracting it from the initial level. Patterns of aerobic biotransformation were consistent with those observed in Experiment A. Zero order rates of aerobic biotransformation appeared higher in this experiment because the aerobic periods were shorter, permitting use of only the earliest (and steepest) segment of the mass loss curves for rate determination.

PS-6 Gasoline with No Oxygenates. Table 6-1 provides a summary of results for the aerobic period of this set. Mass loss curves are shown in Figure 6-2. Microcosms in this set lost 1.087 mg/L total BTEX in the first week of incubation. This loss corresponded to the complete depletion of oxygen within the microcosms. Toluene and m-xylene had the greatest mass losses during the aerobic period, followed by o- and p- xylene, and ethylbenzene. No biotransformation of benzene was observed. Once oxygen was below detection in the microcosms, there was no detectable biotransformation of any of the monoaromatics.

Table 6-1. Summary of Results: Aerobic Period of Experiment B - Limited Oxygen Microcosms for PS-6 Gasoline with No Oxygenates (incubation period: 420 days; initial dissolved oxygen: 7.48 mg/L; aerobic period: <7 days)

Compound	Initial Conc. (µg/L)	Mass Lost (%)	Mass Lost (µg/L)	Zero Order Biotrans. Rate (µg/L/day)
Benzene	4803	<DL	<DL	--
Toluene	2585	13	336	48
Ethylbenzene	338	17	58	8
p-Xylene	328	34	112	16
m-Xylene	800	55	440	63
o-Xylene	523	27	141	20
Total BTEX	9377	12	1087	155

PS-6 Gasoline with 15% MtBE. Table 6-2 provides a summary of results for the three week aerobic period of this experiment. A

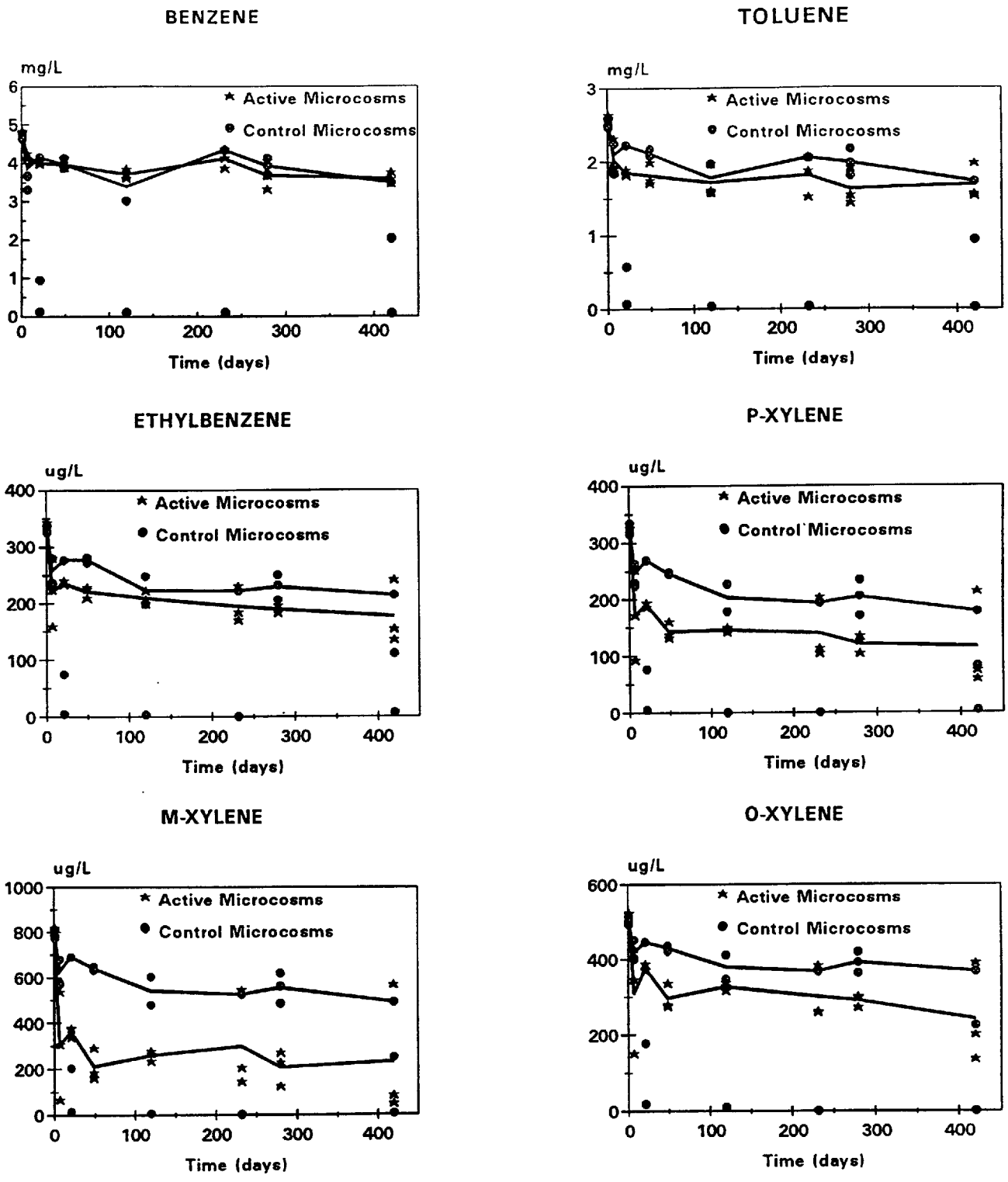

Figure 6-2. BTEX persistence in limited oxygen microcosms; PS-6 gasoline with no oxygenates (aerobic period: 7 days)

mass loss curve for MtBE is shown in Figure 6-3, and Figure 6-4 depicts BTEX persistence in the microcosms.

Table 6-2. Summary of Results: Aerobic Period Experiment B -Limited Oxygen Microcosms of PS-6 Gasoline with 15% MtBE (incubation period: 420 days; initial dissolved oxygen: 7.48 mg/L; aerobic period: <21 days)

Compound	Initial Conc. (µg/L)	Mass Lost (%)	Mass Lost (µg/L)	Zero Order Biotrans. Rate (µg/L/day)
Benzene	4807	<DL	<DL	--
Toluene	2741	20	548	39
Ethylbenzene	355	29	103	7
p-Xylene	352	49	173	12
m-Xylene	863	71	613	44
o-Xylene	568	35	199	14
Total BTEX	9686	17	1636	116
MtBE	315,000	<DL	<DL	--

There were no losses of MtBE discernable in the aerobic or the anaerobic period which could be attributed to biodegradation. On the final sampling date of the experiment, MtBE concentrations were low in both the active and sterile replicates probably due to volatilization during a one-month waiting period for sample analysis.

Biotransformation of about 1.636 mg/L BTEX occurred during the aerobic period of incubation. Overall, the patterns of aerobic biotransformation of the monoaromatics were nearly identical to those in the no oxygenates case, with toluene and m-xylene exhibiting the greatest mass losses, and benzene completely recalcitrant.

During the anaerobic period, there was no discernable biotransformation of the monoaromatics, except perhaps a small benzene loss at the final sampling session. However, a black

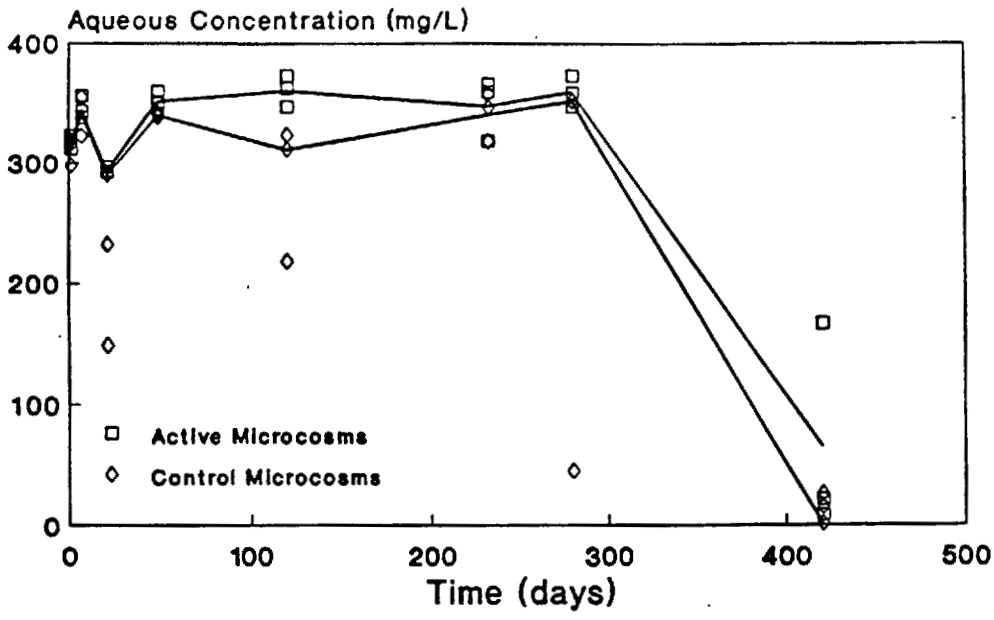

Figure 6-3. MtBE persistence in limited oxygen microcosms of PS-6 gasoline with 15% MtBE

precipitate had appeared in the microcosms by Day 420. The precipitate was probably ferrous sulfide, which, along with a hydrogen sulfide smell in the microcosms, indicated sulfate reducing bacteria had become active.

PS-6 Gasoline with 15% Methanol. Table 6-3 summarizes results for the three-week aerobic period of incubation and Figures 6-5 and 6-6 depict mass loss curves for the solutes. Active microcosms in this set lost 1.45 mg/L total BTEX during the aerobic period. Patterns of aerobic biotransformation were similar to those in the no oxygenates and 15% MtBE cases, except toluene losses were significantly smaller. There was a one-week acclimation period for the toluene in this set, which shortened the time available for its aerobic biotransformation.

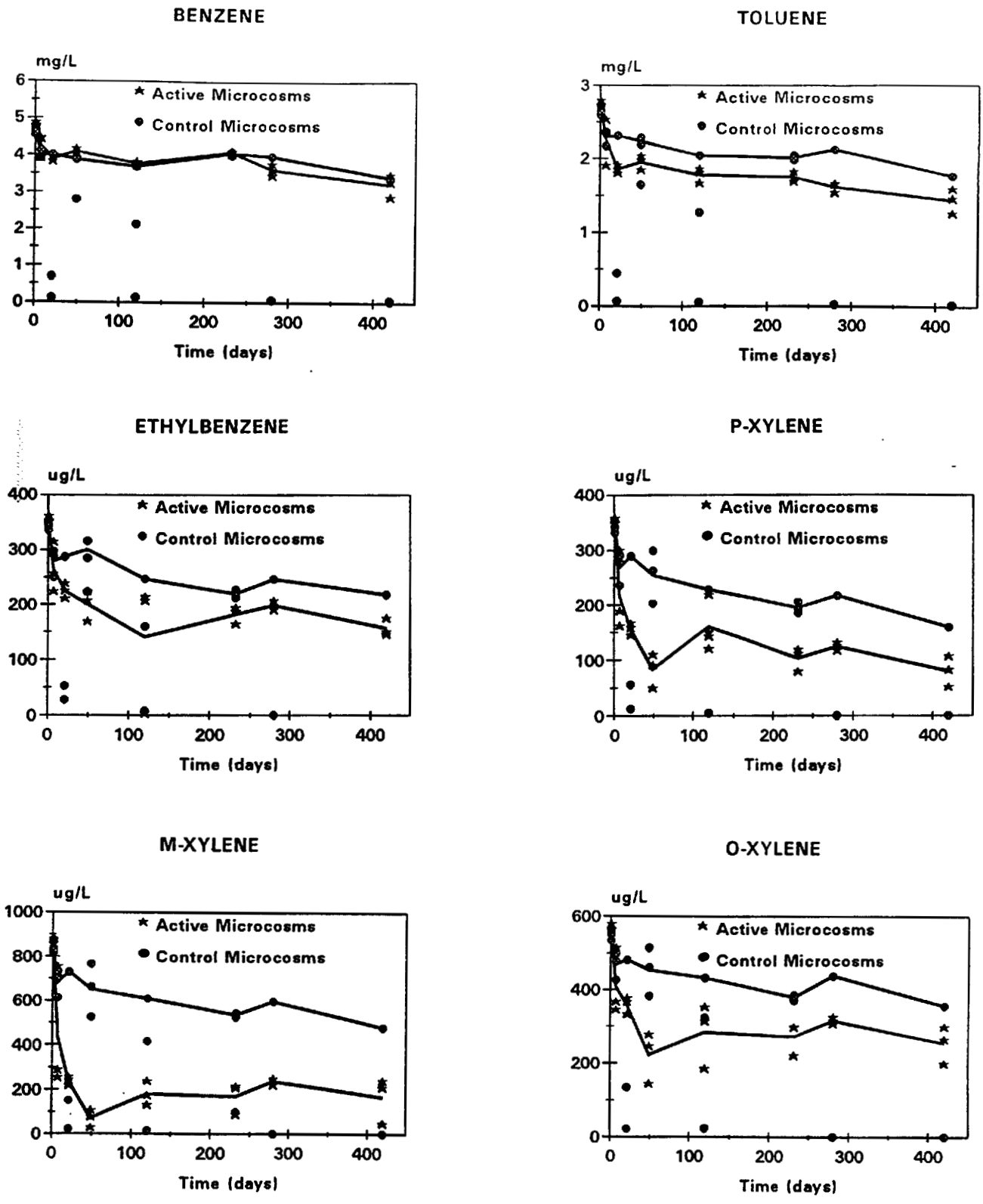

Figure 6-4. BTEX persistence in limited oxygen microcosms of PS-6 gasoline with 15% MtBE (aerobic period: 21 days)

Table 6-3. Summary of Results: Aerobic Period Experiment B: Limited Oxygen Microcosms of PS-6 Gasoline with 15% Methanol (incubation period: 420 days; initial dissolved oxygen: 7.48 mg/L; aerobic period: <21 days)

Compound	Initial Conc. (µg/L)	Mass Lost (%)	Mass Lost (µg/L)	Zero Order Biotrans. Rate (µg/L/day)
Benzene	5068	<DL	<DL	--
Toluene	2847	9	256	18
Ethylbenzene	373	22	82	6
p-Xylene	366	45	165	12
m-Xylene	896	80	717	63
o-Xylene	575	40	230	16
Total BTEX	10143	14	1450	115
Methanol	997,000	<DL	<DL	--

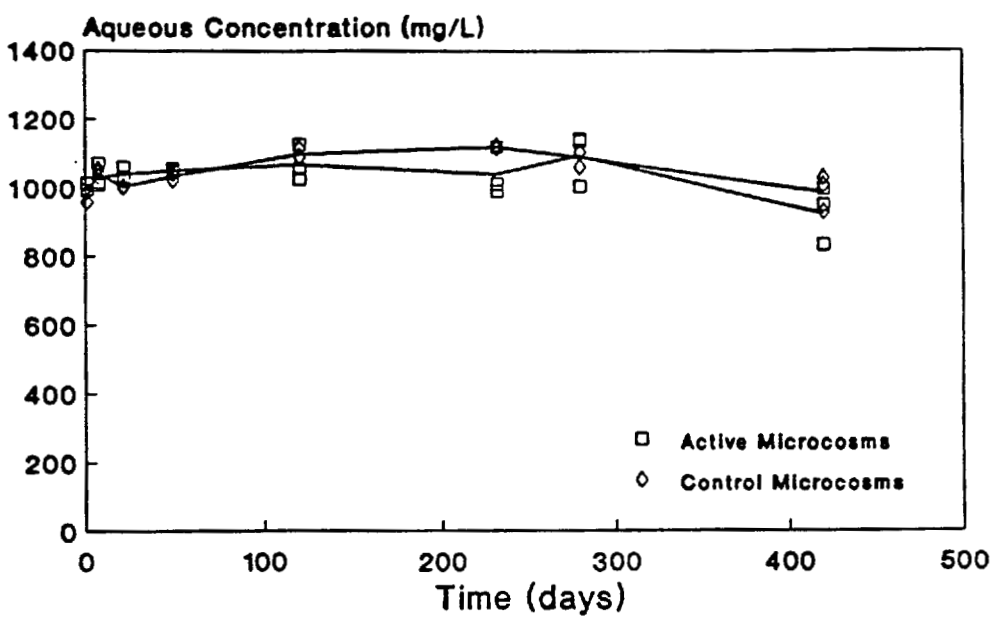

Figure 6-5. Methanol persistence in limited oxygen microcosms of PS-6 gasoline with 15% methanol.

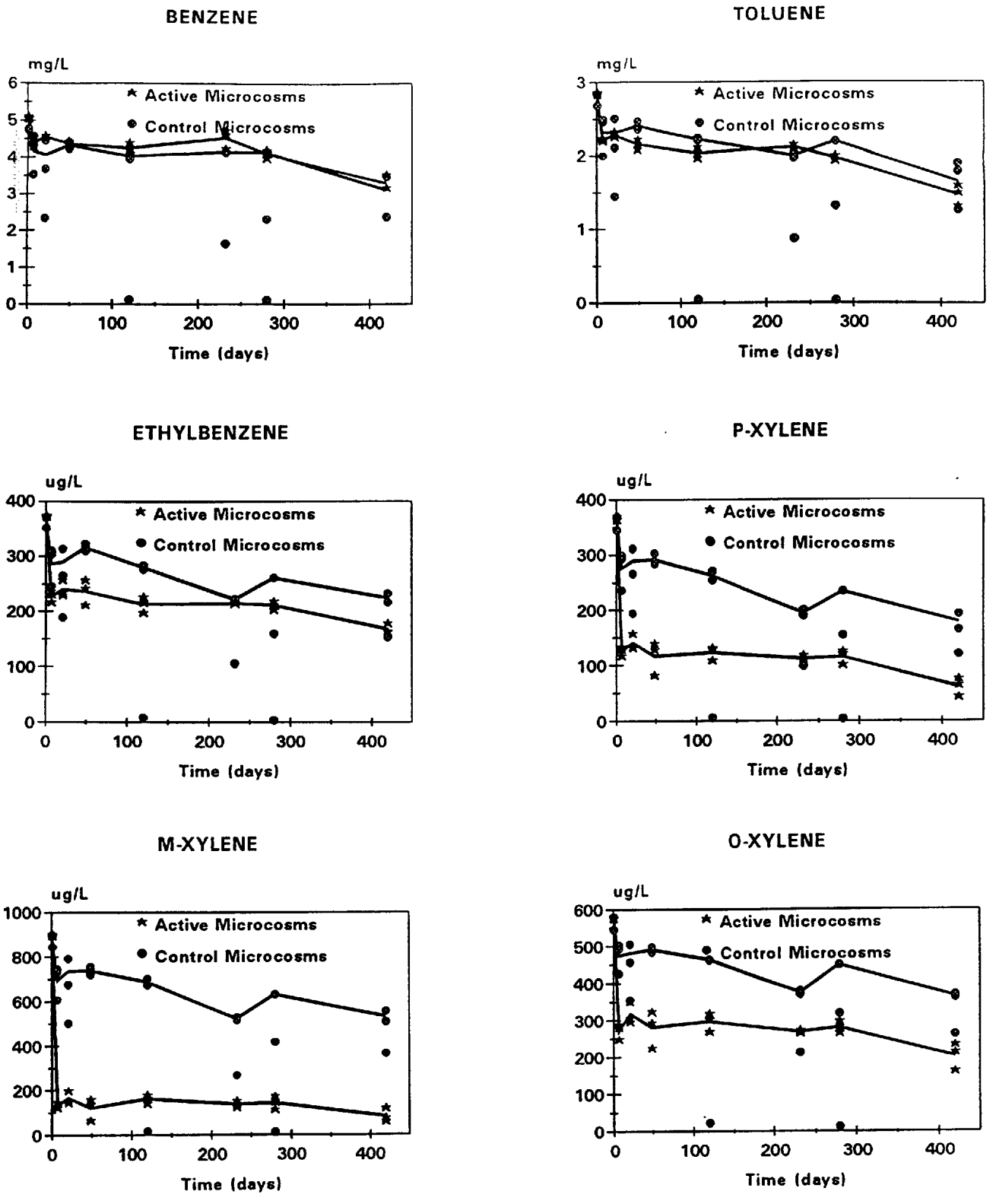

Figure 6-6. BTEX persistence in limited oxygen microcosms of PS-6 gasoline with 15% methanol (aerobic period: 21 days)

No methanol biotransformation was observed during the aerobic period of incubation. However, there was only sufficient oxygen available to mineralize about 5 mg/L. Since this concentration represents only 0.5% of the initial methanol level, aerobic methanol loss would not have been detectable.

There were no detectable losses of BTEX during the anaerobic period. The black precipitate observed in the 15% MtBE microcosms on Day 420 was observed in this set by Day 120. The appearance of the black precipitate corresponded to an apparent 5% loss in methanol. Although this represents a small percentage it is larger than the variability in the control data for methanol. It represents a substantial mass loss - about 50 mg/L, five times the total BTEX present in the microcosms.

PS-6 Gasoline with 85% Methanol. This set of microcosms is not directly comparable to the baseline case because the BTEX concentrations were significantly higher. Table 6-4 summarizes results for the aerobic period. Figure 6-7 illustrates the persistence of the methanol the microcosms, and Figure 6-8 depicts BTEX mass loss curves.

Table 6-4. Summary of Results: Aerobic Period Experiment B - Limited Oxygen Microcosms of PS-6 Gasoline with 85% Methanol (incubation period: 278 days; initial dissolved oxygen: 7.28 mg/L; aerobic period: <48 days)

Compound	Initial Conc. (µg/L)	Mass Lost (%)	Mass Lost (µg/L)	Zero Order Biotrans. Rate (µg/L/day)
Benzene	7225	<DL	<DL	--
Toluene	4728	<DL	<DL	--
Ethylbenzene	598	<DL	<DL	--
p-Xylene	577	<DL	<DL	--
m-Xylene	1482	<DL	<DL	--
o-Xylene	907	<DL	<DL	--
Total BTEX	15,517	<DL	<DL	--
Methanol	7,432,000	<DL	<DL	--

Methanol losses were not detected during the aerobic or the anaerobic period of the experiment. The oxygen level in the microcosms was sufficient to permit biotransformation of only 5 mg/L of methanol (about 0.07% of the initial concentration), so aerobic biotransformation is unlikely to have been observed. By Day 188, a black precipitate had developed in the unsterilized microcosms, indicating that sulphate reducers had become active.

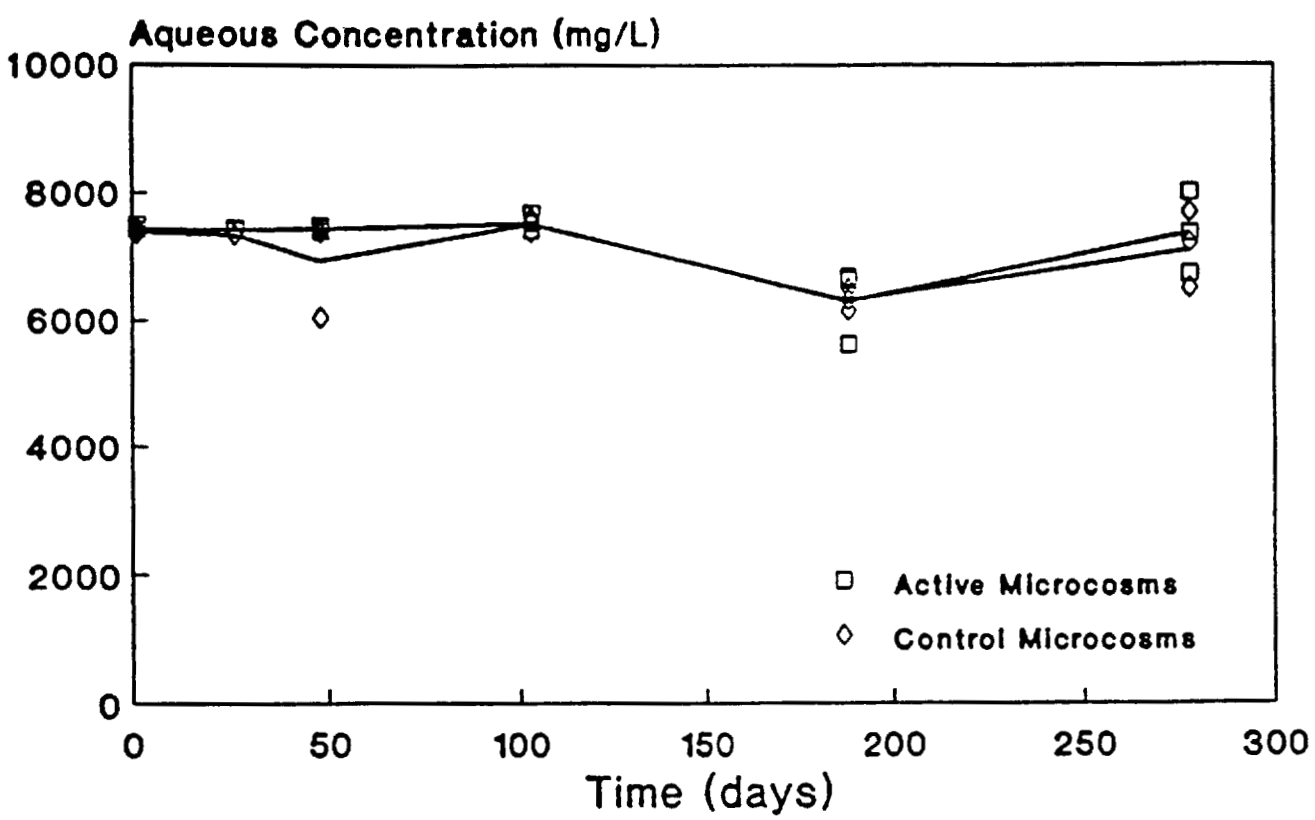

Figure 6-7. Methanol persistence in limited oxygen microcosms of PS-6 gasoline with 85% methanol

No BTEX losses were observed during the aerobic period. This finding is consistent with the results of Experiment A, in which the acclimation period for benzene, toluene, and the xylenes was greater than 103 days, and for ethyl benzene was about 54 days. The Experiment B aerobic period was only 48 days: by the time the compounds had acclimatized, oxygen was no longer available as an electron acceptor. During the anaerobic period of this experiment, no BTEX mass losses were observed.

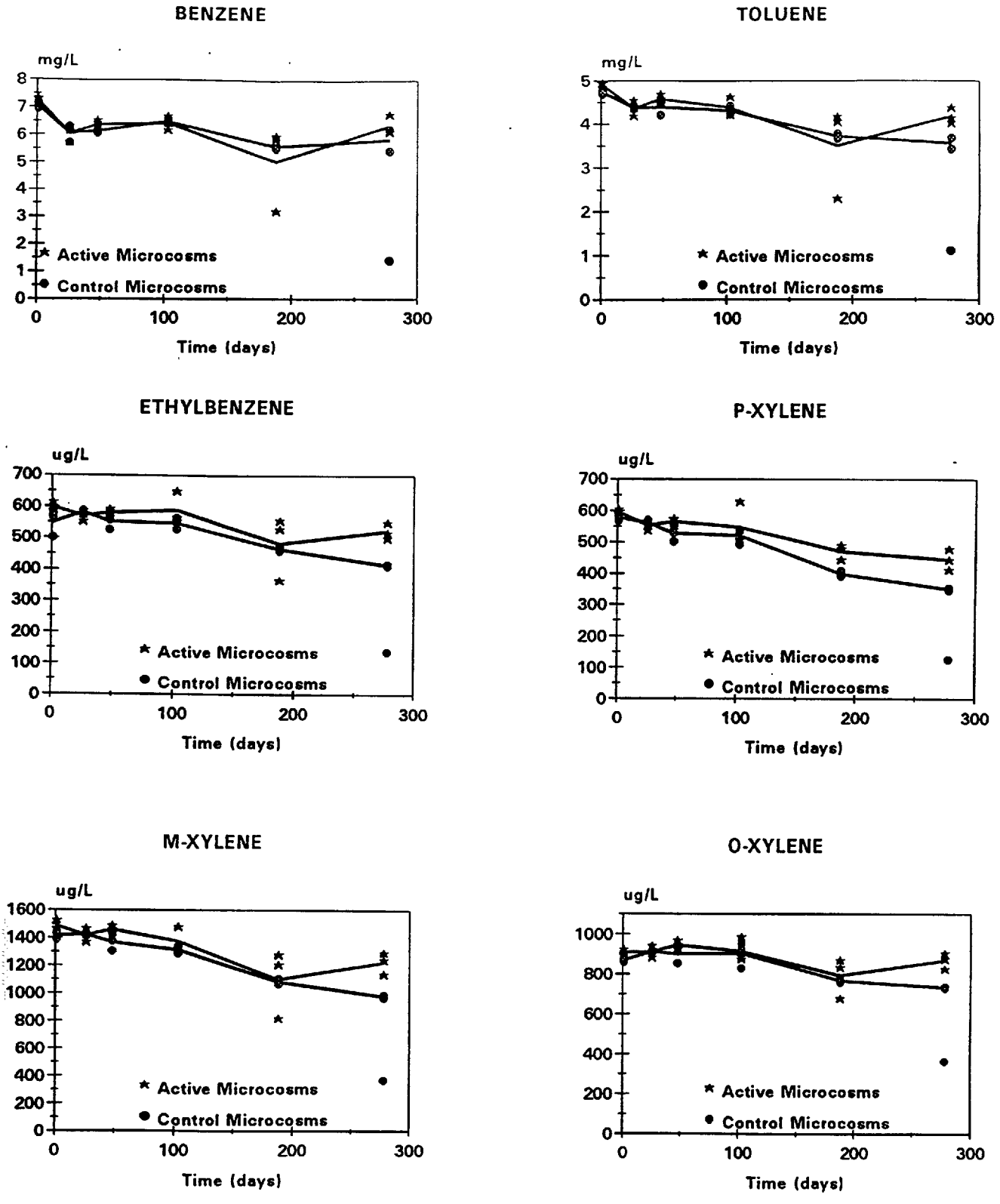

Figure 6-8. BTEX persistence in limited oxygen microcosms of PS-6 gasoline with 85% methanol (aerobic period: 48 days)

Section 7

DISCUSSION

This section summarizes the effects of methanol and MtBE on biotransformation of the monoaromatics and explores the role of oxygen in BTEX and oxygenate persistence.

7.1 Biotransformation of the Monoaromatics

The persistence of the monoaromatics in microcosms containing no oxygenates varied depending on the availability of oxygen. Under conditions of unlimited oxygen, BTEX biodegraded rapidly, and no acclimation period was observed for any of the compounds. Most of the mass loss occurred within the first two months. The substituted monoaromatics were below detection by the end of the study. Benzene persisted at low concentrations and remained at 10 µg/L (twice the drinking water limit) after an eight-month incubation period.

In general, the rate of aerobic biotransformation was similar for all six compounds. The range of biotransformation rates, about 2 to 15 µg/L/day (zero order) or 0.24 to 0.38 day^{-1} (first order), compares favorably with those observed in previous microcosm studies of the biodegradation of monoaromatic gasoline constituents in Borden groundwater (Berry-Spark et. al., 1988).

Minor differences in aerobic biotransformation rates for the compounds included a slightly more rapid loss for toluene and m-xylene, and a slightly slower loss for benzene. More rapid biotransformation of m-xylene relative to the other xylenes has also been reported by Kappeler and Wuhrman (1978). The meta isomer is apparently more susceptible to microbial attack in some environments. The small variations in relative rate of biotransformation for the compounds of this study had little effect on their overall persistence when oxygen availability was not a constraint.

Under oxygen-limited conditions, biotransformation of the monoaromatics was observed during the aerobic period only, and oxygen was depleted in the microcosms within one week. No BTEX mass losses were detected during the subsequent fifteen-month anaerobic period. At the end of the experiment, concentrations of all of the monoaromatics remained above 100 µg/L. Berry-Spark (1987) also observed aerobic biotransformation of the monoaromatics followed by anaerobic recalcitrance in oxygen-limited Borden microcosms.

The initial dissolved oxygen within the microcosms of this study was approximately 7.5 mg/L. Assuming all of the oxygen was used solely for mineralization of the monoaromatics, a loss of approximately 2.4 mg/L would be necessary to cause anoxic conditions. Mass losses of only 1.087 mg/L of these compounds corresponded with the development of anoxia, indicating that at least some of the oxygen was used for metabolism of other solutes.

Demands for oxygen could come from other dissolved constituents of the gasoline or from the naturally occurring organic carbon content in the water or the soil. Low molecular weight, readily metabolizable aliphatic hydrocarbons constitute a large fraction of the total organic carbon in PS-6 gasoline-contacted groundwater (Brookman et. al.,1985): these represent a likely source of the oxygen demand.

The microbial population in the limited oxygen microcosms was unable to transform a measurable quantity of benzene before oxygen was depleted, so benzene persisted at the initial concentration throughout the fifteen-month study. It has been hypothesized that benzene ring cleavage may be particularly difficult for certain microbes to achieve because there are no methyl groups present to disrupt the electron symmetry of the ring (Gibson and Subramanian, 1984). These results lend support to this theory.

In contrast, toluene and m-xylene appear to have been favored by the microbes. Biotransformation of these two compounds was rapid during the aerobic period, accounting for over 70% of the total mass loss observed for the monoaromatics. M-xylene persisted at a concentration of less than half of its initial level throughout the subsequent anaerobic period. Toluene persisted at a greater level due to its higher initial concentration.

These findings suggest that the early susceptibility of a monoaromatic compound to microbial attack bears a strong relation to its level of persistence in an oxygen-limited setting. For compounds of equivalent susceptibility, the level of persistence depends on the magnitude of the initial concentration.

7.2 Persistence and Impact of MtBE

In both the unlimited oxygen and limited oxygen experiments, MtBE was recalcitrant over incubation periods of eight to fifteen months. This lack of observable biotransformation can be viewed as an extended acclimation period. Given a longer contact time, the Borden microbial population might eventually gain the ability to consume a detectable quantity of MtBE. Experiments designed to evaluate MtBE biotransformation at lower initial concentrations could provide further information about the fate of this compound.

The absence of detectable MtBE biotransformation over the experimental timeframe was not unexpected. Several authors have reported that the ether bond is resistent to microbial attack (Harada and Nagashima, 1975). Jensen (1989) conducted microcosm studies using a mineral-rich medium and a variety of inocula including Borden sand and waste treatment sludge, and saw no MtBE degradation in a series of 60-day experiments. Thomas et. al. (1988) provided limited evidence of minor biotransformation of MtBE in oxygen-limited microcosms after four weeks of incubation. Experiments of longer duration have not been reported.

MtBE appears to have had little influence on BTEX persistence. Regardless of oxygen availability, biotransformation of the monoaromatics in the presence of MtBE was similar to that in the baseline case with no oxygenates. Minor deviations included less tailing of the mass loss curves for the substituted monoaromatics when oxygen was unlimited, and slightly greater mass losses for these compounds in the limited oxygen experiments.

7.3 Persistence and Impact of Methanol

Like MtBE, methanol was relatively recalcitrant in both the unlimited oxygen and limited oxygen experiments although some anaerobic methanol biotransformation may have occurred following acclimation periods of at least 100 days. Tests of longer duration should be conducted to evaluate this possibility. The possible anaerobic biotransformation of methanol coincided with formation of a black precipitate in the hypovials, indicating sulphate reducers had become active. Although sulphate reducing bacteria are strict anaerobes and their growth is inhibited in the presence of oxygen, sulphate reduction has been reported in aerobic soils (Grant and Long, 1981), suggesting that the sulphate reducers can survive in aerobic systems. The presence of methanol appears to enhance the activity of these organisms: in baseline microcosms with no oxygenates, no black precipitate was observed.

Hickman and Novak (1989) reported findings that were similar to those of this study: methanol biotransformation followed an acclimation period of greater than 100 days in static, limited oxygen microcosms incubated at 10°C. White (1986) reported complete biotransformation of 1000 mg/L methanol within one year at a 10°C incubation temperature in oxygen limited microcosms. White observed both the formation of a black precipitate and production of methane, and attributed the methanol biotransformation in his study to a combination of sulphate reduction and fermentation.

Under unlimited oxygen conditions, the influence of methanol on biotransformation of the monoaromatics depended on the initial concentration of methanol. The data from the 85% methanol microcosms provide strong evidence that high concentrations of methanol (7,000 mg/L) can significantly increase the persistence of BTEX. The acclimation periods for the substituted monoaromatics were extended by eight to fifteen weeks, and the subsequent biotransformation rates were dramatically reduced relative to the baseline case with no oxygenates. No biotransformation of benzene was observed over a ten-month incubation period, indicating substantial inhibition of the benzene degraders.

The extension of the BTEX acclimation periods may be due to toxic effects of the methanol: Ingram and Buttke (1984) report that alcohols can cause bacterial killing by disrupting the cellular permeability barrier. If portions of the Borden microbial population were killed off or metabolically inhibited by the methanol, the long acclimation periods can be viewed as extended "recovery" periods, after which the microbes are again capable of degrading BTEX. Alternatively, the microbes may be preferentially transforming methanol at a rate that is below detection. Regardless of the mechanism of inhibition, the results indicate that BTEX persistence may be prolonged on the order of years in the presence of high methanol levels, even when oxygen is plentiful.

At the lower methanol concentration of 1000 mg/L (15% methanol microcosms), the biodegradation rates of toluene, ethyl benzene, and the xylenes were slightly enhanced compared to the case of gasoline with no oxygenates. Toluene and ethyl benzene acclimation periods increased by about a week, but their overall persistence was slightly shorter than in the baseline microcosms due to the increased rates of biotransformation. In contrast, benzene appeared recalcitrant.

Based on the combined results of the 15% methanol and 85% methanol experiments, it can be hypothesized that there may be a threshold concentration above which methanol impedes the biotransformation of the substituted monoaromatics and below which the biotransformation of these compounds is enhanced. It would be necessary to conduct further experiments with a variety of methanol concentrations to gain a clearer understanding of the range of potential effects of this compound on biotransformation of the monoaromatics when oxygen availability is not limiting factor.

Under limited oxygen conditions, the effects of methanol on BTEX persistence were more significant. Oxygen was depleted in the 15% methanol microcosms in less than three weeks and in the 85% methanol microcosms within about seven weeks. Sufficient oxygen was available in the microcosms to mineralize about 2.4 mg/L BTEX. However, loss of only 1.45 mg/L of the substituted monoaromatics coincided with the development of anoxia in the 15% methanol microcosms, while no BTEX biotransformation was observed during the aerobic period in the 85% methanol microcosms.

Other possible sources of oxygen demand include the aliphatic gasoline components, naturally occuring organic matter, or the methanol. The source of the oxygen demand is probably not the methanol, since the duration of the aerobic period was longer in microcosms containing methanol than in those with no oxygenates. It is possible that the methanol may even have hindered biotransformation of some of the aliphatics.

The depletion of the oxygen in the microcosms magnified both the beneficial and the adverse effects of methanol on BTEX biotransformation. The enhanced rate of aerobic biotransformation for the xylenes in the presence of 1000 mg/L methanol resulted in a substantial loss of mass of these compounds in the aerobic period of the limited oxygen experiment.

Once conditions became anaerobic, all three xylene isomers persisted, but at significantly lower concentrations than in comparable microcosms with no oxygenates.

Inhibitory effects of the methanol were also magnified under limited oxygen conditions. At 1000 mg/L, methanol presence caused a one-week increase in acclimation period for toluene. The increase had little bearing on toluene persistence in the unlimited oxygen microcosms because the subsequent rate of biotransformation was rapid. However, under limited oxygen conditions, the one-week acclimation period had greater significance because it was large relative to the duration of the aerobic period. Less toluene mass was consumed during the aerobic period, and the toluene persisted at higher concentrations than in the baseline case with no oxygenates. In the 85% methanol microcosms, no BTEX biotransformation was detected. The increased acclimation periods induced by the methanol extended beyond the seven week aerobic period of the experiment, and no subsequent anaerobic biotransformation was observed.

These findings suggest that small changes in acclimation period induced by methanol presence will have little influence on the long-term persistence of the monoaromatics in settings where oxygen availability is not a constraint. However, small increases in acclimation period, even on the order of days or weeks, are of much greater consequence in an oxygen-limited setting. At high methanol concentrations (7000 mg/L), the combined effects of methanol presence and oxygen limitation serve to significantly constrain BTEX metabolism, causing their long-term recalcitrance.

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APPENDIX HA

ANALYTICAL METHODS AND QUALITY CONTROL

HEXANE MICRO-EXTRACTION FOR THE DETERMINATION OF PURGEABLE AROMATICS IN GROUNDWATER

A hexane liquid-liquid micro-extraction/gas chromatographic technique has been devised as a rapid alternative to the slower purge and trap and conventional solvent extraction methods for the determinations of benzene, toluene, and the three xylene isomers at trace levels in groundwater. Split injection isothermal capillary column chromatography permits a run time of five minutes without the loss of baseline resolution. Method detection limits in µg/L were as follows: benzene, 1.8; toluene, 1.4; p-xylene, 0.6; m-xylene, 0.8; o-xylene, 1.2. Replicate analyses of an in-house quality control standard containing approximately 85 µg/L of each compound were accumulated during a typical 8-day session. The means of the determinations differed no more than 1% from the true values with relative standard deviations averaging 2.9% overall. Evaluation of a USEPA quality control standard spiked into a typical organic-free groundwater matrix gave similar results.

INTRODUCTION

A gas chromatographic technique is described to determine several aromatic components of gasoline in groundwater samples. The components are: benzene, toluene, ethylbenzene and p-, m-, and o-xylene. Usually these compounds are determined by purge and trap techniques (1). However, because the hydrogeologist may require many analyses, purge and trap methods are too time consuming to use on a routine basis. Separatory funnel or continuous solvent extraction techniques are not only slow and labor intensive, but can suffer from volatilization losses as well. The methodology presented here was derived from a pentane liquid-liquid extraction (LLE) technique previously described by Glaze *et al.*(1983), which requires that the partitioning of an analyte be at equilibrium between the two phases, as opposed to being exhaustively extracted from the water (2). Pentane was replaced

with hexane since the chromatographic column used easily affords complete separation of the analytes from the solvent peak. This helps to reduce the solvent vapor pressure in the sample vials thereby improving the precision of the method.

EXPERIMENTAL

Apparatus

Samples and aqueous standards were extracted in Supelco 18-ml crimp-top hypo-vials with teflon-faced silicone septa. The determinations were performed on an isothermal gas chromatograph equipped with a split injection port, capillary column, and FID. The column used was a 0.32mm x 6m fused quartz type with a 0.25 µm bonded CARBOWAX 20M stationary phase. The chromatographic conditions were as follows:

injection port temperature: 200°C;
oven temperature: 90° C;
carrier gas: Helium;
column flow rate: 5 ml/min.

Reagents

The following reagents were used:

glass distilled hexane and methanol;
organic-free reagent water;
10% aqueous sodium azide solution
reagent grade benzene, toluene, m-fluorotoluene, p-, m-, o-xylenes.

PROCEDURES

Sample Bottle Preparation

Bottles and other glassware were soaked in a commercial alkaline cleaning solution for several hours, then rinsed with deionized water, dilute nitric acid, and more deionized water. The bottled were then baked overnight at 110°C. Upon removal from the oven, the bottles were covered with foil. Because the septa can be a major source of contamination, they were boiled in water for one hour, then baked overnight at 110°C in an oven.

Sample Collection and Handling

Sample vials were filled to overflowing with no aeration, quickly crimped, then stored on ice until needed. Prior to capping, 100 µl of the sodium azide preservative was injected directly into the water. The same treatment was given to the aqueous standards. To solvent extract a sample or standard, a vent needle was inserted through the septum, then 1 ml of water was removed with a syringe. With the vent still in place, 500 µl of hexane, containing the internal standard m-fluorotoluene, was added. The vent was then removed and the bottle agitated on its side at maximum speed on a platform shaker for 10 min. The bottle was inverted and the phases allowed to separate for 10 to 30 minutes before the sample was analyzed. The bottle was then set upright and approximately 4 µl of the hexane phase was removed, while venting, for injection into the chromatograph.

Quality Control

Samples and standards were equilibrated to room temperature before extraction. The gas chromatograph was calibrated at the start of each working day by averaging the runs for three standard replicates at approximately 3000 µg/L for each compound. Two stock standards, one approximately an order of magnitude more concentrated than the other, were independently prepared. The higher concentration was used to calibrate the instrument; the lower one was used as a check, and was routinely run after every tenth sample. The standard checks were initially prepared gravimetrically, injecting the various pure compounds through a septum into one 60 ml aliquot of methanol. This solution was then further diluted volumetrically by injecting through a septum into one liter of reagent water.

An upper limit of 1% (v/v) methanol in water has been previously recommended; however, it was not necessary to exceed 0.05% for the present study (2). The aqueous standard dilution was mixed

on a magnetic stirrer to avoid aeration, and then quickly distributed into hypovials with an all-glass and teflon repipette. The methanolic standards were stored in a freezer when not in use and discarded after 3 months. Aqueous standards were stored no longer than two days. The hexane extraction solution and reagent water blanks were checked on a daily basis.

RESULTS AND DISCUSSION

Method Detection Limit (MDL)

Table 1 shows detection limits for the analytical procedure. It does not take into account field sampling errors, sample matrix, or analyte losses due to long term volatilization. These values were determined by the procedure recommended by USEPA/EMSL which defines MDL as the minimum concentration measurable with 99%confidence that it is greater than zero (3).

Accuracy and Precision

Near the detection limit, it can be seen that for the six compounds, the average absolute error is approximately +13%. The overall standard deviation at this level is 9.4% Table 2 summarizes the results of replicate analyses of inhouse quality control samples accumulated during a typical sampling session (n=31). As expected, at these higher concentrations the overall standard deviation has improved to 2.9%, while accuracy is virtually 100%. To further evaluate the method and its applicability to field samples, a USEPA quality control standard (WP 879 #1) was analyzed in a typical groundwater matrix. Calibration standards were prepared as previously described using laboratory reagent water. The results shown in Table 3 display standard deviations comparable to those obtained previously with errors which are generally larger, but still acceptable. It is quite likely that this increase in error was a result of experimenter bias, not matrix effects, as the ionic strength of the groundwater used was much lower than the 1.0 required to affect extraction efficiencies, while the Ph was neutral (1).

CONCLUSIONS

The hexane micro-extraction method has a sensitivity approaching that of a purge and trap system, but can be used routinely, with a much shorter turnaround time. This allows the analyst to work with larger batches of samples at a faster rate. Detection limits are adequate with a simple split injection, eliminating the need to employ more elaborate splitless or cryogenic schemes. These limits can be lowered somewhat by increasing the water to hexane ratio.

The column used is capable of resolving the p- and m-xylene isomers in a 5 min. isothermal run. Separation of these two isomers is impossible with the less polar capillary columns commonly employed. Furthermore, the method can easily be extended to include ethylbenzene and various halogenated aromatics.

Samples containing organic interferents (e.g. waste water, landfill leachate) require the replacement of the FID with a detector which is more specific to the compounds of interest (e.g. a MSD).

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(2) Glaze, W.H., C.C. Lin, J.L. Burleson, J.E. Henderson, D. Mapel, R. Rawley, D.R. Scott. *Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water*, Project Report, Contract No's. CR-805472, CR-808561; USEPA/EMSL:Cincinatti, OH, 1983.

(3) *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, EPA-600/4-82-057; Longbottom, J.E., J.J. Lichtenberg, J. James, Eds.; USEPA/EMSL:Cincinatti, OH, 1982; Appendix A.

Table 1. Method Detection Limit

Compound	N	S%	X	X_o	E%	MDL
Benzene	7	13	4.3 ± 0.7	3.7	+16	1.8
Toluene	7	13	3.2 ± 0.5	3.6	-11	1.4
p-Xylene	7	5.8	3.1 ± 0.2	3.6	-14	0.6
m-Xylene	7	5.7	4.4 ± 0.3	3.7	+19	0.8
o-Xylene	7	9.7	3.8 ± 0.4	3.7	+3	1.2

N = number of replicate determinations; S% = relative standard deviation; X = mean of replicate determinations, 99% confidence level, background subtracted; X_o = true value; E% = average relative error, reagent water matrix. Concentrations are in µg/L.

Table 2. Accuracy and Precision at Typical Sample Concentrations

Compound	N	S%	X	X_o	E%
Benzene	31	4.2	84.5 ± 1.9	85.2	-1
Toluene	31	2.9	83.8 ± 0.9	83.7	0
p-Xylene	31	2.4	83.3 ± 1.5	83.5	0
m-Xylene	31	2.8	86.2 ± 1.5	85.6	+1
o-Xylene	31	2.0	86.6 ± 1.6	85.7	+1

Solutions made in reagent water matrix.
Concentrations are in µg/L.

Table 3. Analysis of USEPA Quality Control Sample WP 879 #1

Compound	N	S%	X	X_o	E%
Benzene	7	3.0	30.6 ± 1.1	30.7	0
Toluene	7	6.1	5.6 ± 0.4	4.1	+37
p-Xylene	7	1.8	20.5 ± 0.4	19.1	+7
m-Xylene	7	1.7	45.3 ± 0.9	42.6	+6
o-Xylene	7	2.5	12.1 ± 0.4	10.6	+14

X_o = EPA value, groundwater matrix. Concentrations are in µg/L.

DIRECT AQUEOUS INJECTION PROCEDURE

OXYGENATES:
- MtOH - Methanol
- EtOH - Ethanol
- MTBE - Methyl Tertiary Butyl Ether
- TAME - Tertiary Amyl Methyl Ether
- IPE - Iso-propyl Ether

SAMPLE PREPARATION

A 1.0ml aqueous sample (removed from a 18.0ml hypovial for BTEX analysis) is placed in a 1.5ml screw cap septum vial and sealed with a teflon lined septa and screw cap. A 4ul aliquot of the aqueous solution is sampled for chromatographic analysis using a 10ul syringe equipped with a chaney adapter to enhance repeatability.

CHROMATOGRAPHIC ANALYSIS

The aqueous samples are run on a Hewlett Packard 5840A gas chromatograph with a FID detector. The column is 10ft. X .125 in. i.d., packed with 3% SP1500 on Carbopack B (80/100 mesh). The analyses are run isothermally at 100, 190 or 200°C, depending on oxygenate (see chart). A helium carrier gas at a flow rate of 20 ml/min is used. The detector temperature is 300°C and the injection temperature is 200°C.

Quantitative results are determined using an ESTD method of calibration and method detection limits for some of the compounds are found to be <250ug/L, using the EPA procedure for method detection limit (MDL).

GC COLUMN TEMPERATURES (ISOTHERMAL)

Oxygenate	Column Temp °C	Retention Time
MTBE	190	3.0
IPE	190	4.0
EtOH	120	1.8
TAME	200	4.0
MtOH	100	1.4

DIRECT AQUEOUS INJECTION - OXYGENATES

METHOD DETECTION LIMIT

Oxygenate	N	X (mg/L)	Xo	S%	E%	MDL
MtOH	12	.760+/-.039	.988	5.13	-23.1	.106
MTBE	12	.533+/-.093	.740	17.4	-28.0	.249

* MDL for the other oxygenates are estimated to be in the same range as those reported.

ACCURACY AND PRECISION AT TYPICAL CONCENTRATION

OXYGENATE	N	X (mg/L)	Xo	S%	E%
MtOH	21	409.92+/-8.73	395.00	2.13	+3.78
MTBE	21	71.95+/-1.31	74.0	1.81	-2.77

N : number of replicate determinations

X : mean of replicate determinations, 99% confidence level

Xo : true value

S% : relative standard deviation

E% : relative error

MDL : method detection limit

APPENDIX HB

CALCULATION OF AQUEOUS PHASE CONCENTRATIONS

The concentrations of the monoaromatics from Experiment A were measured in the headspace and were converted to the equivalent equilibrium aqueous concentrations. Headspace data were obtained at different temperatures, so regression equations for variation in Henry's constants with temperature (Ashworth et. al., 1988) were used for the conversions. The equations have the form:

$$H_{cc} = e^{\left[A - \frac{B}{T}\right]}$$

where:

H_{cc} is Henry's Law constant in units of (atm m^3/mol),
T is the temperature in K,
A and B are constants differing for each chemical whose values are given by Ashworth et al. (1988) and are presented below:

Compound	A	B
Benzene	5.534	3194
Toluene	5.133	3024
Ethylbenzene	11.92	4994
p-Xylene	6.931	3520
m-Xylene	6.280	3337
0-Xylene	5.541	3220

The Henry's Law constants thus obtained were converted to concentration-based constants (H_{pc}) through the equation:

$$H_{pc} = \frac{H_{cc}}{R\,T}$$

where:

H_{pc} is the Henry's Law Constant in (mol/m^3)/(mol/m^3),
H_{cc} is the Henry's Law Constant in (atm m^3)/mol,
R is the ideal gas constant, 8.2056 X 10^{-5} (atm m^3)/(mol K),
T is the temperature in K.

Table 4-2 shows these Henry's Law constants for various temperatures of concern.

Table 4-2. Henry's Law Constants ((mol/m^3)/ (mol/m^3))

Compound	**20°C**	**25°C**	**26°C**	**27°C**
Benzene	0.20	0.23	0.24	0.25
Toluene	0.23	0.27	0.28	0.29
Ethylbenzene	0.25	0.33	0.34	0.36
p-Xylene	0.26	0.31	0.32	0.34
m-Xylene	0.25	0.30	0.31	0.32
o-Xylene	0.18	0.21	0.22	0.23

APPENDIX HC

DATA FOR EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

DATA

Key to Chemicals:

B	Benzene	METH	Methanol
T	Toluene	MTBE	Methyl-tert-butyl-ether
E	Ethylbenzene		
M-XYL	m-Xylene		
O-XYL	o-Xylene		
P-XYL	p-xylene		

<DL : Less than the detection limit
N/A : Not analyzed

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

PS-6 GASOLINE WITH 15% METHANOL
Headspace Concentrations for the Monoaromatics
Biologically Active Microcosms

DAY	BENZENE (ug/L)	TOLUENE (ug/L)	ETHYL-BENZENE (ug/L)	p-XYL (ug/L)	m-XYL (ug/L)	o-XYL (ug/L)
1	526	305	40	36	95	46
1	520	302	40	36	95	46
1	535	312	41	37	98	48
7	753	434	57	49	114	63
7	519	306	38	29	58	41
7	653	373	46	35	64	47
14	486	109	3	<DL	<DL	<DL
14	518	93	2	<DL	<DL	<DL
14	529	150	6	<DL	<DL	<DL
21	585	3	<DL	<DL	<DL	<DL
21	672	49	<DL	<DL	<DL	<DL
21	645	89	<DL	<DL	<DL	<DL
51	522	<DL	<DL	<DL	<DL	<DL
51	526	<DL	<DL	<DL	<DL	<DL
51	524	<DL	<DL	<DL	<DL	<DL
69	457	<DL	<DL	<DL	2	<DL
69	588	3	<DL	<DL	<DL	<DL
69	447	<DL	<DL	<DL	<DL	<DL
114	217	<DL	<DL	<DL	<DL	<DL
114	324	<DL	<DL	<DL	<DL	<DL
114	322	<DL	<DL	<DL	<DL	<DL
232	329	1	<DL	<DL	<DL	<DL
232	297	<DL	<DL	<DL	<DL	<DL
232	307	<DL	<DL	<DL	<DL	<DL

Mean Concentrations (ug/L)

1	527	306	40	36	96	47
7	642	370	47	38	79	50
14	511	117	3	<DL	<DL	<DL
21	634	47	<DL	<DL	<DL	<DL
51	524	<DL	<DL	<DL	<DL	<DL
69	497	1	<DL	<DL	1	<DL
114	288	<DL	<DL	<DL	<DL	<DL
232	311	<DL	<DL	<DL	<DL	<DL

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

PS-6 GASOLINE WITH 15% METHANOL
Headspace Concentrations for the Monoaromatics
Sterile Control Microcosms

DAY	BENZENE (ug/L)	TOLUENE (ug/L)	ETHYL-BENZENE (ug/L)	p-XYL (ug/L)	m-XYL (ug/L)	o-XYL (ug/L)
1	563	331	44	40	104	50
1	565	332	44	39	105	50
1	595	349	47	42	111	53
7	630	381	51	46	123	59
7	529	325	44	40	107	56
7	752	445	59	52	140	68
14	419	245	31	27	72	37
14	484	283	37	33	88	41
14	460	272	36	31	83	40
21	717	421	56	50	131	63
21	611	362	48	43	112	54
21	702	409	55	48	128	61
51	616	355	48	42	114	56
51	628	369	50	43	119	58
51	656	391	53	46	127	63
69	682	399	52	44	128	60
69	532	314	41	34	102	50
69	685	400	53	44	127	60
114	538	310	40	33	93	45
114	481	271	35	28	29	39
114	553	314	41	34	93	43
232	565	314	40	32	92	44
232	549	303	38	29	85	42
232	440	222	26	20	58	29

Mean Concentrations (ug/L)

1	574	337	45	40	107	51
7	637	384	51	46	123	61
14	454	266	34	30	81	39
21	677	397	53	47	124	60
51	633	372	50	44	120	59
69	633	371	49	41	119	57
114	524	298	39	32	72	42
232	518	280	34	27	79	38

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

PS-6 GASOLINE WITH 85% METHANOL
Headspace Concentrations for the Monoaromatics
Biologically Active Microcosms

DAY	BENZENE (ug/L)	TOLUENE (ug/L)	ETHYL-BENZENE (ug/L)	p-XYL (ug/L)	m-XYL (ug/L)	o-XYL (ug/L)
1	940	707	99	89	235	104
1	922	694	98	88	233	101
1	924	699	99	89	236	103
7	851	643	91	81	218	97
7	914	689	97	86	231	102
7	884	665	93	82	223	97
15	816	591	78	67	193	88
15	763	556	71	63	180	82
15	824	590	77	67	190	87
26	830	585	77	63	182	83
26	790	570	76	65	191	88
26	851	609	80	69	200	92
35	811	568	74	64	179	81
35	788	564	73	63	178	83
35	787	563	73	63	179	82
54	823	577	74	64	179	83
54	781	559	71	62	173	80
54	731	530	68	60	167	77
103	815	570	67	60	170	80
103	795	559	52	59	174	84
103	808	591	70	68	190	86
278	698	480	50	52	156	71
278	695	461	47	48	110	65
278	774	473	<DL	55	138	77

Mean Concentrations (ug/L)

1	928	670	99	89	234	103
7	883	666	94	83	224	99
15	801	579	76	66	188	86
26	824	588	78	65	191	88
35	795	565	73	64	179	82
54	778	555	71	62	173	80
103	806	573	63	62	178	83
278	722	471	32	52	135	71

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

PS-6 GASOLINE WITH 85% METHANOL
Headspace Concentrations for the Monoaromatics
Sterile Control Microcosms

DAY	BENZENE (ug/L)	TOLUENE (ug/L)	ETHYL-BENZENE (ug/L)	p-XYL (ug/L)	m-XYL (ug/L)	o-XYL (ug/L)
1	920	701	100	90	237	103
1	903	685	99	89	233	101
1	861	647	92	82	218	97
7	930	697	98	86	230	100
7	886	667	95	84	224	99
7	922	690	97	85	229	102
15	877	632	84	71	204	92
15	858	622	82	70	199	91
15	745	538	74	62	180	81
26	813	570	71	61	176	78
26	762	554	75	63	181	82
26	846	614	83	70	199	94
35	812	575	77	65	183	82
35	802	567	76	64	182	81
35	807	571	77	65	180	82
54	742	537	73	61	173	79
54	790	563	76	65	179	84
54	806	570	76	65	180	83
103	773	549	73	60	170	80
103	783	559	74	61	174	82
103	825	582	78	65	181	88
278	618	457	65	55	153	80
278	747	506	67	54	153	81
278	759	537	78	68	177	96

Mean Concentrations (ug/L)

1	895	677	97	87	229	100
7	913	684	96	85	228	100
15	827	597	80	68	194	88
26	807	579	76	64	185	85
35	807	571	77	65	182	82
54	779	557	75	64	177	82
103	793	563	75	62	175	83
278	708	500	70	59	161	86

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

PS-6 GASOLINE WITH 15% MTBE
Headspace Concentrations for the Monoaromatics
Biologically Active Microcosms

DAY	BENZENE (ug/L)	TOLUENE (ug/L)	ETHYL-BENZENE (ug/L)	p-XYL (ug/L)	m-XYL (ug/L)	o-XYL (ug/L)
1	579	348	46	42	109	53
1	561	334	44	41	106	51
1	582	350	46	42	111	54
7	419	239	30	29	57	37
7	216	124	15	11	25	21
7	481	274	35	20	71	43
14	184	19	<DL	<DL	<DL	<DL
14	373	144	14	10	7	12
14	420	212	26	22	36	31
21	420	155	14	8	3	10
21	501	239	30	26	45	37
21	383	152	17	15	16	21
51	309	3	<DL	<DL	<DL	<DL
51	225	<DL	<DL	<DL	<DL	<DL
51	216	31	2	<DL	<DL	<DL
69	<DL	<DL	<DL	<DL	3	<DL
69	291	16	<DL	<DL	<DL	<DL
69	310	45	<DL	<DL	2	<DL
114	<DL	<DL	<DL	<DL	<DL	<DL
114	52	<DL	<DL	<DL	<DL	<DL
114	<DL	<DL	<DL	<DL	<DL	<DL
232	<DL	<DL	<DL	<DL	<DL	<DL
232	14	<DL	<DL	<DL	<DL	<DL
232	<DL	<DL	<DL	<DL	<DL	<DL

Mean Concentrations (ug/L)

1	574	344	45	42	108	53
7	372	212	27	20	51	34
14	326	125	13	11	14	14
21	435	182	20	17	21	22
51	250	11	1	<DL	<DL	<DL
69	200	20	<DL	<DL	1	<DL
114	17	<DL	<DL	<DL	<DL	<DL
232	5	<DL	<DL	<DL	<DL	<DL

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

PS-6 GASOLINE WITH 15% MTBE
Headspace Concentrations for the Monoaromatics
Sterile Control Microcosms

DAY	BENZENE (ug/L)	TOLUENE (ug/L)	ETHYL-BENZENE (ug/L)	p-XYL (ug/L)	m-XYL (ug/L)	o-XYL (ug/L)
1	608	365	48	44	116	57
1	626	377	49	46	120	61
1	635	383	51	47	123	60
7	427	261	33	39	81	44
7	603	362	46	42	112	56
7	522	319	41	37	99	51
14	475	294	40	36	95	48
14	546	332	43	39	105	51
14	666	397	52	46	122	58
21	529	326	42	38	101	50
21	608	377	50	46	122	61
21	567	331	40	35	96	48
51	610	374	50	44	130	61
51	544	336	45	40	117	57
51	548	338	45	40	110	57
69	563	331	42	36	107	52
69	460	276	36	30	90	50
69	685	400	53	44	127	60
114	418	249	32	27	76	39
114	451	269	34	29	81	43
114	513	305	40	35	96	46
232	512	292	37	30	85	42
232	517	295	37	30	85	42
232	513	293	37	30	85	42

Mean Concentrations (ug/L)

1	623	375	49	45	120	59
7	517	314	40	39	98	50
14	563	341	45	40	107	52
21	568	345	44	40	106	53
51	567	350	46	41	119	58
69	570	336	44	37	108	54
114	461	274	35	30	84	42
232	514	293	37	30	85	42

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

PS-6 GASOLINE WITH NO OXYGENATES
Headspace Concentrations for the Monoaromatics
Biologically Active Microcosms

DAY	BENZENE (ug/L)	TOLUENE (ug/L)	ETHYL-BENZENE (ug/L)	p-XYL (ug/L)	m-XYL (ug/L)	o-XYL (ug/L)
1	356	192	25	21	57	27
1	379	206	27	23	62	29
1	406	221	29	25	67	32
7	431	216	29	25	57	38
7	505	250	34	30	63	42
7	553	289	38	33	83	47
14	253	103	15	15	22	21
14	398	183	26	23	47	34
14	410	174	24	21	35	29
21	346	152	21	21	47	31
21	396	166	22	22	46	32
21	441	199	26	25	51	34
51	136	10	<DL	<DL	<DL	<DL
51	344	4	<DL	<DL	<DL	<DL
51	308	32	<DL	<DL	<DL	<DL
69	257	74	8	8	7	8
69	144	45	5	8	10	8
69	10	<DL	<DL	<DL	<DL	<DL
114	39	9	<DL	<DL	<DL	<DL
114	<DL	<DL	<DL	<DL	<DL	<DL
114	19	<DL	<DL	<DL	<DL	<DL
232	<DL	<DL	<DL	<DL	<DL	<DL
232	7	<DL	<DL	<DL	<DL	<DL
232	<DL	<DL	<DL	<DL	<DL	<DL

Mean Concentrations (ug/L)

1	380	207	27	23	62	29
7	496	251	33	29	68	42
14	354	153	21	20	35	28
21	394	172	23	23	48	33
51	263	15	<DL	<DL	<DL	<DL
69	137	40	4	5	6	6
114	19	3	<DL	<DL	<DL	<DL
232	2	<DL	<DL	<DL	<DL	<DL

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

PS-6 GASOLINE WITH NO OXYGENATES
Headspace Concentrations for the Monoaromatics
Sterile Control Microcosms

DAY	BENZENE (ug/L)	TOLUENE (ug/L)	ETHYL-BENZENE (ug/L)	p-XYL (ug/L)	m-XYL (ug/L)	o-XYL (ug/L)
1	475	261	33	29	79	38
1	448	247	32	29	76	36
1	420	234	30	27	73	36
7	703	407	55	48	131	61
7	623	364	49	44	119	57
7	683	394	53	47	125	61
14	581	331	44	39	104	48
14	496	280	38	33	87	41
14	608	344	45	40	106	50
21	669	374	49	43	114	53
21	529	303	40	36	95	47
21	604	338	44	39	102	49
51	589	329	43	37	102	50
51	664	372	49	43	118	59
51	616	335	48	42	114	56
69	574	323	43	35	102	48
69	569	325	43	36	104	49
69	591	332	44	37	107	50
114	513	280	36	30	81	38
114	449	252	33	27	76	37
114	483	265	34	28	80	39
232	517	280	36	29	82	40
232	501	269	34	26	76	37
232	445	244	31	25	71	34

Mean Concentrations (ug/L)

1	448	247	32	28	76	37
7	670	389	52	46	125	60
14	562	318	42	37	99	46
21	600	339	44	39	104	50
51	623	345	47	41	111	55
69	578	327	43	36	104	49
114	482	265	34	28	79	38
232	488	264	34	27	76	37

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

CO_2 AND O_2 IN MICROCOSMS
Headspace Concentrations for Biologically Active Microcosms

DAY	PS-6 GASOLINE		15% METHANOL & PS-6		85% METHANOL & PS-6		15% MTBE & PS-6	
	CO2 %	O2 %	CO2 %	O2 %	CO2 %	O2 %	CO2 %	O2 %
1	0.17	20.98	0.16	20.3	0.11	21.8	0.16	21.6
1	0.15	20.86	0.72	20.3	0.11	21.3	0.16	21.9
1	0.16	20.86	0.14	20.9	0.11	20.9	0.16	21.2
7	0.08	21.59	0.10	21.4	0.11	20.7	0.07	19.6
7	0.09	21.93	0.06	21.4	0.11	18.9	0.06	20.7
7	0.07	22.26	0.07	20.6	0.16	21.4	0.08	22.6
14	0.24	22.39	0.21	20.5	0.14	21.9	0.24	20.8
14	0.23	22.64	0.27	14.9	0.13	20.9	0.25	21.5
14	0.29	23.57	0.23	19.9	0.24	20.9	0.17	20.8
21	0.27	22.57	0.35	21.3	0.14	21.6	0.30	21.8
21	0.29	21.90	0.33	20.4	0.12	20.3	0.32	26.6
21	0.25	20.55	0.27	19.7	0.11	18.2	0.29	26.3
51	0.43	N.A.	0.40	20.9	0.36	21.1	0.42	21.7
51	0.40	22.13	0.41	20.8	0.32	18.2	0.36	19.5
51	0.48	20.46	0.39	20.5	0.33	22.0	0.42	22.5
69	0.43	19.75	0.42	20.3	0.42	21.6	0.32	20.3
69	0.39	20.13	0.49	20.3	0.35	18.0	0.41	20.5
69	0.47	19.75	0.37	20.3	0.30	19.7	0.36	20.9
114	0.44	19.24	0.41	19.5	0.09	21.3	0.48	19.0
114	0.46	19.24	0.43	19.2	0.36	15.7	0.48	18.8
114	0.47	19.24	0.44	19.5	0.32	16.1	0.48	19.0
232	0.23	19.57	0.24	19.6	0.53	19.3	0.21	19.7
232	0.21	19.57	0.20	19.7	0.51	17.6	0.23	20.1
232	0.23	19.31	0.12	19.3	0.68	16.2	0.22	21.0

AVERAGE PERCENT (%)

1	0.16	20.90	0.34	20.5	0.11	21.3	0.16	21.6
7	0.08	21.93	0.08	21.1	0.13	20.3	0.07	20.9
14	0.25	22.87	0.24	18.4	0.17	21.2	0.22	21.0
21	0.27	21.67	0.32	20.5	0.12	20.0	0.30	24.9
51	0.44	21.30	0.40	20.7	0.34	20.4	0.40	21.2
69	0.43	19.88	0.43	20.3	0.36	19.8	0.36	20.6
114	0.46	19.24	0.43	19.4	0.26	17.7	0.48	18.9
232	0.22	19.48	0.19	19.5	0.57	17.7	0.22	20.3

EXPERIMENT A: UNLIMITED OXYGEN MICROCOSMS

CO_2 AND O_2 IN MICROCOSMS
Headspace Concentrations for Sterile Control Microcosms

DAY	PS-6 GASOLINE		15% METHANOL & PS-6		85% METHANOL & PS-6		15% MTBE & PS-6	
	CO2 %	O2 %	CO2 %	O2 %	CO2 %	O2 %	CO2 %	O2 %
1	0.08	21.56	0.08	21.6	0.10	21.4	0.08	21.4
1	0.09	21.21	0.08	20.7	0.10	20.8	0.10	21.1
1	0.10	21.21	0.08	21.7	0.09	20.1	0.08	21.9
7	0.04	19.56	0.04	22.3	0.19	20.7	0.04	22.9
7	0.03	21.93	0.05	22.3	0.10	21.3	0.05	22.6
7	0.05	N.A.	0.05	22.3	0.15	21.0	0.05	23.6
14	0.06	22.02	0.08	21.3	0.08	21.5	0.06	21.3
14	0.06	20.91	0.07	21.3	0.08	21.6	0.07	22.2
14	0.08	22.95	0.10	22.2	0.08	21.6	0.07	20.2
21	0.08	22.24	0.09	21.6	0.05	20.9	0.08	26.3
21	0.06	21.80	0.07	20.8	0.05	21.4	0.10	22.6
21	0.10	20.48	0.09	20.9	0.06	19.7	0.10	23.7
51	0.08	20.46	0.09	23.8	0.08	21.5	0.07	21.3
51	0.07	20.63	0.07	20.9	0.05	19.3	0.08	22.1
51	0.08	21.71	0.09	22.6	0.09	22.3	0.07	21.7
69	0.08	20.89	0.09	21.3	0.10	21.6	0.07	20.9
69	0.07	20.13	0.08	20.9	0.11	21.0	0.08	20.5
69	0.08	20.70	0.08	21.1	0.11	21.0	0.07	20.7
114	0.09	19.49	0.09	20.2	0.06	21.0	0.08	20.2
114	0.08	19.97	0.07	20.5	0.04	21.5	0.08	19.7
114	0.08	19.46	0.09	19.5	0.03	22.0	0.08	19.2
232	0.09	22.27	0.10	21.4	0.06	18.1	0.09	21.4
232	0.09	21.63	0.09	21.1	0.06	16.6	0.08	21.2
232	0.09	21.95	0.10	21.2	0.07	18.1	0.08	20.1

AVERAGE PERCENT (%)

1	0.09	21.33	0.08	21.3	0.10	20.8	0.09	21.5
7	0.04	20.75	0.05	22.3	0.15	21.0	0.05	23.1
14	0.07	21.96	0.08	21.6	0.08	21.6	0.07	21.2
21	0.08	21.51	0.08	21.1	0.05	20.7	0.09	24.2
51	0.08	20.93	0.08	22.4	0.07	21.0	0.07	21.7
69	0.08	20.57	0.08	21.1	0.11	21.2	0.07	20.7
114	0.08	19.65	0.08	20.0	0.04	21.5	0.08	19.7
232	0.09	21.95	0.10	21.2	0.06	17.6	0.08	20.9

APPENDIX HD

EXPERIMENT B - LIMITED OXYGEN MICROCOSMS DATA

Key to Chemicals:

O_2	Oxygen
METH	Methanol
MTBE	Methyl-tert-butyl-ether
B	Benzene
T	Toluene
E	Ethylbenzene
M-XYL	m-Xylene
O-XYL	o-Xylene
P-XYL	p-Xylene

PS-6 GASOLINE

DAY	B	T	E	P-XYL	M-XYL	O-XYL	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L
Active Microcosms							
1	4785.6	2579.7	336.1	326.5	802.4	520.5	5.2
1	4793.3	2553.4	335.4	324.6	782.5	523.5	
1	4829.7	2622.7	342.7	332.9	817.1	523.4	
7	4125.6	2307.6	280.6	252.2	535.3	428.3	<DL
7	4247.2	1862.0	224.3	171.2	305.1	346.3	
7	4124.5	1893.3	158.5	92.8	65.4	149.9	
21	4040.7	1813.8	233.6	185.5	335.9	372.5	<DL
21	3979.1	1843.5	233.8	192.4	372.9	370.9	
21	3974.0	1886.3	240.3	193.1	374.7	386.8	
49	4118.9	1982.3	225.1	130.7	158.8	273.9	<DL
49	3874.7	1700.5	209.6	136.2	183.4	277.3	
49	3890.5	1743.5	228.6	159.3	289.4	336.0	
120	3835.3	1962.4	222.1	148.8	232.1	336.3	<DL
120	3678.4	1594.6	206.7	145.9	264.7	328.6	
120	3597.3	1574.5	199.3	140.9	275.5	315.6	
232	4337.4	2054.0	229.8	202.3	542.6	382.5	<DL
232	4120.3	1866.4	183.2	103.4	142.4	259.8	
232	3853.6	1509.4	169.1	112.0	202.7	258.0	
280	4036.0	1903.6	194.8	103.4	122.7	271.2	<DL
280	3667.7	1532.9	189.1	124.4	226.7	296.9	
280	3301.0	1431.9	182.3	133.6	268.5	301.0	
420	3742.5	1969.1	240.9	213.4	566.7	388.8	<DL
420	3460.6	1554.8	153.3	73.4	81.8	199.2	
420	3565.0	1527.6	134.0	58.7	47.0	135.8	

DAY	B	T	E	P-XYL	M-XYL	O-XYL	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L
Mean Concentrations							
1	4802.9	2585.2	338.1	328.0	800.7	522.5	5.2
7	4165.7	2021.0	221.2	172.0	301.9	308.2	<DL
21	3997.9	1847.9	235.9	190.3	361.2	376.7	<DL
49	3961.3	1808.8	221.1	142.1	210.5	295.7	<DL
120	3703.7	1710.5	209.3	145.2	257.4	326.8	<DL
232	4103.8	1809.9	194.1	139.2	295.9	300.1	<DL
280	3668.2	1622.8	188.7	120.5	205.9	289.7	<DL
420	3589.4	1683.8	176.1	115.2	231.8	241.3	<DL
Control Microcosms							
1	4776.4	2578.4	337.5	334.5	812.0	513.3	N/A
1	4672.8	2488.3	326.4	314.7	771.2	500.7	
1	4617.8	2462.8	326.2	320.9	779.2	491.3	
7	4078.0	2242.0	280.2	263.7	678.7	450.7	N/A
7	3307.8	1840.7	232.0	224.5	568.7	399.6	
7	3675.2	1942.6	237.1	229.5	579.1	404.6	
21	4154.6	2221.0	276.8	269.4	690.2	445.2	N/A
21	938.8	572.8	74.6	76.5	203.4	176.9	
21	117.2	68.1	5.0	4.9	14.6	17.8	
49	3892.4	2071.5	272.7	244.3	632.5	422.2	N/A
49	3878.0	2078.7	279.1	248.7	646.8	429.3	
49	4135.3	2163.8	281.5	244.5	642.6	435.8	

DAY	B	T	E	P-XYL	M-XYL	O-XYL	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L
120	3013.0	1579.9	199.1	177.8	477.3	347.1	N/A
120	106.7	33.1	3.0	0.0	5.7	9.6	
120	3758.1	1964.8	248.7	226.7	602.7	410.5	
232	83.2	32.8	0.0	0.0	3.7	0.0	N/A
232	96.5	36.3	0.0	0.0	0.0	0.0	
232	4326.7	2049.8	222.4	192.7	523.4	367.7	
280	3689.5	1801.4	205.5	170.4	483.4	364.0	N/A
280	4123.1	2162.4	250.1	234.0	617.0	418.5	
280	3937.7	1975.6	232.4	205.5	562.1	391.5	
420	3485.1	1728.0	214.1	177.3	490.0	367.9	N/A
420	2026.7	939.7	110.1	81.9	249.6	224.3	
420	63.8	19.9	6.7	4.0	5.9	<DL	
Mean Concentrations							
1	4689.0	2509.9	330.0	323.4	787.4	501.8	
7	3687.0	2008.4	249.8	239.2	608.8	418.3	
21	1736.9	954.0	118.8	116.9	302.7	213.3	
49	3968.6	2104.7	277.8	245.8	640.6	429.1	
120	2292.6	1192.6	150.2	134.8	361.9	255.7	
232	1502.1	706.3	74.1	64.2	175.7	122.6	
280	3916.8	1979.8	229.3	203.3	554.2	391.3	
420	1858.6	895.9	110.3	87.8	248.5	197.4	

85% METHANOL AND PS-6 GASOLINE

DAY	B	T	E	P-XYL	M-XYL	O-XYL	METH	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L
Active Microcosms								
1	7312.4	4922.6	594.6	595.3	1461.4	907.8	7413.7	5.4
1	7094.8	4842.5	586.7	589.7	1464.2	894.2	7398.8	
1	7266.2	4935.2	611.9	603.2	1521.4	920.3	7483.1	
26	6133.4	4362.3	573.3	555.9	1419.7	911.9	7420.7	0.3
26	6283.3	4530.7	586.6	567.7	1463.4	938.9	7403.5	
26	5703.2	4179.2	552.0	535.5	1367.3	879.6	7436.0	
48	6123.6	4461.6	564.3	551.9	1434.7	922.4	7424.7	<DL
48	6483.0	4674.5	591.4	571.4	1486.1	965.5	7474.7	
48	6389.6	4575.5	586.4	573.0	1457.9	944.8	7380.5	
103	6653.8	4622.0	648.3	627.7	1477.7	983.0	7408.6	<DL
103	6391.1	4314.2	553.0	508.5	1307.4	881.9	7512.1	
103	6135.4	4213.4	564.1	504.6	1337.9	871.4	7670.9	
188	5939.2	4161.5	555.4	489.0	1273.9	866.5	6671.7	<DL
188	3177.2	2282.5	363.1	443.1	813.9	676.0	5623.8	
188	5861.9	4040.8	528.3	477.9	1202.4	832.0	6633.4	
278	6077.3	4018.6	499.6	412.8	1134.1	824.0	6715.1	<DL
278	6115.1	4143.3	517.8	443.1	1237.4	872.8	7999.2	
278	6731.8	4375.5	549.9	477.9	1289.6	901.7	7353.4	
Mean Concentrations								
1	7224.5	4900.1	597.7	596.0	1482.3	907.4	7431.9	5.4
26	6040.0	4357.4	570.6	553.0	1416.8	910.1	7420.1	0.3
48	6332.1	4570.5	580.7	565.4	1459.6	944.2	7426.6	<DL
103	6393.4	4383.2	588.4	546.9	1374.3	912.1	7530.5	<DL
188	4992.8	3494.9	482.3	470.0	1096.8	791.5	6309.6	<DL
278	6308.1	4179.1	522.4	444.6	1220.4	866.2	7355.9	<DL

DAY	B	T	E	P-XYL	M-XYL	O-XYL	METH	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L
Control Microcosms								
1	7137.4	4765.7	577.3	578.4	1422.0	866.4	7355.7	N/A
1	6951.7	4732.8	500.4	584.3	1440.1	875.0	7430.6	
1	6981.2	4686.9	566.7	567.2	1385.7	858.0	7338.8	
26	6133.4	4400.6	584.0	570.1	1432.6	914.9	7332.5	N/A
26	6283.3	4336.5	575.4	547.5	1408.2	904.2	7328.7	
26	5703.2	4362.2	587.4	566.9	1428.2	917.5	7326.8	
48	6123.8	4207.5	526.4	501.4	1304.3	852.0	7369.0	N/A
48	6044.6	4451.3	558.1	528.6	1377.6	911.8		
48	6114.6	4490.1	573.9	552.7	1421.2	930.4	7367.1	
103	6544.2	4424.5	563.7	537.1	1308.5	924.8	7373.8	N/A
103	6394.7	4271.9	549.2	532.0	1286.2	827.9	7531.3	
103	6395.9	4228.1	528.0	492.0	1338.0	951.1	7608.5	
188	5572.9	3665.1	461.8	393.6	1069.3	757.9	6157.9	N/A
188	5487.4	3697.8	460.1	393.0	1066.7	758.5	6326.1	
188	5616.5	3774.2	474.0	408.9	1103.7	778.9	6494.3	
278	5406.8	3441.5	412.8	353.4	985.6	736.1	7690.4	N/A
278	1398.4	1108.8	136.6	126.0	366.8	363.4	7201.6	
278	6193.5	3682.2	417.0	344.8	966.9	727.8	6503.1	
Mean Concentrations								
1	7023.4	4728.5	548.1	576.6	1415.9	866.5	7375.0	
26	6040.0	4366.4	582.3	561.5	1423.0	912.2	7329.3	
48	6094.3	4383.0	552.8	527.6	1367.7	898.1	7368.0	
103	6444.9	4308.2	547.0	520.4	1310.9	901.3	7504.5	
188	5558.9	3712.4	465.3	398.5	1079.9	765.1	6326.1	
278	4332.9	2744.2	322.2	274.7	773.1	609.1	7131.7	

15% METHANOL AND PS-6 GASOLINE

DAY	B	T	E	P-XYL	M-XYL	O-XYL	METH	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L
Active Microcosms								
1	5033.4	2827.8	371.3	363.1	890.9	576.6	1009.4	6.8
1	5109.1	2860.5	373.2	364.7	898.0	574.2	991.9	
1	5061.4	2851.5	374.2	369.4	898.1	574.3	990.7	
7	4521.5	2217.7	231.2	132.6	145.8	280.0	1013.3	1.0
7	4372.3	2193.5	216.9	116.6	119.7	247.5	1067.8	
7	4277.7	2234.2	236.1	127.8	126.1	286.9	1005.5	
21	4584.4	2256.2	233.4	131.0	143.5	304.9	1026.4	<DL
21	4549.6	2326.1	257.3	156.6	195.9	350.0	1030.3	
21	4483.0	2249.9	229.6	133.0	152.3	295.2	1056.7	
49	4322.6	2219.0	257.0	139.3	157.0	322.7	1050.3	<DL
49	4298.1	2159.0	241.9	127.5	134.9	292.0	1043.0	
49	4415.1	2079.7	211.4	81.6	64.2	224.4	1053.6	
120	4366.6	1957.4	197.4	108.9	138.1	268.5	1056.0	<DL
120	4076.0	2029.6	215.6	127.9	164.0	300.8	1125.4	
120	4209.5	2108.1	227.0	130.6	177.4	316.7	1025.8	
232	4601.7	2090.6	215.2	117.8	150.9	263.9	1010.7	<DL
232	4702.9	2142.6	214.2	111.0	134.4	272.4	1117.7	
232	4202.0	2098.1	216.4	107.5	121.1	268.6	989.3	
280	4116.5	1987.4	212.0	119.8	142.9	296.0	1002.9	<DL
280	3949.1	1924.1	218.3	124.4	169.2	279.6	1139.9	
280	4173.4	1995.4	202.5	100.2	110.6	264.3	1135.0	
420	3521.9	1592.5	161.3	64.1	73.6	211.6	995.0	<DL
420	3167.3	1310.4	177.3	42.9	57.3	160.3	832.8	
420	3167.8	1495.2	162.7	75.4	116.1	232.0	947.3	

DAY	B	T	E	P-XYL	M-XYL	O-XYL	METH	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L
Mean Concentrations								
1	5067.9	2846.6	372.9	365.7	895.7	575.0	997.3	6.8
7	4390.5	2215.2	228.0	125.7	130.5	271.5	1028.9	1.0
21	4539.0	2277.4	240.1	140.2	163.9	316.7	1037.8	<DL
49	4345.3	2152.6	236.8	116.1	118.7	279.7	1049.0	<DL
120	4217.3	2031.7	213.3	122.5	159.8	295.3	1069.1	<DL
232	4502.2	2110.4	215.3	112.1	135.4	268.3	1039.2	<DL
280	4079.7	1969.0	210.9	114.8	140.9	280.0	1092.6	<DL
420	3285.7	1466.1	167.1	60.8	82.3	201.3	925.0	<DL
Control Microcosms								
1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
1	4768.8	2678.1	351.5	344.6	841.8	544.6	985.9	
1	4737.8	2831.2	371.5	369.4	896.4	579.5	956.6	
7	4377.8	2491.5	310.6	298.9	744.5	502.4	1030.8	N/A
7	3530.5	1999.3	246.0	236.3	607.8	426.5	1053.0	
7	4574.3	2459.2	303.0	293.2	731.3	492.6	1044.0	
21	4442.1	2504.1	313.7	311.3	790.5	504.6	998.7	N/A
21	3675.0	2109.9	265.3	266.3	675.9	456.5	1003.9	
21	2327.5	1446.3	188.0	193.3	500.8	354.2	1003.1	
49	4386.6	2464.7	322.5	302.4	753.7	496.4	1038.6	N/A
49	4276.2	2396.1	314.8	288.0	738.4	492.1	1040.4	
49	4224.5	2353.8	309.8	284.1	719.2	483.4	1020.5	

DAY	B	T	E	P-XYL	M-XYL	O-XYL	METH	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L
120	4080.2	2234.5	276.8	254.2	672.1	462.2	1114.4	N/A
120	113.2	41.6	7.7	6.1	16.0	22.0	1087.1	
120	3939.2	2201.7	284.0	270.4	701.4	462.6	1092.4	
232	4116.3	1969.0	223.0	189.1	513.2	379.5	1120.7	N/A
232	4122.9	2021.7	221.6	199.7	526.3	369.9	1113.2	
232	1630.6	870.1	105.5	98.4	264.8	212.3	1122.9	
280	4115.3	2188.8	261.4	234.7	630.0	449.1	1103.4	N/A
280	95.0	35.8	3.0	4.4	11.7	11.9	1059.2	
280	2292.6	1313.0	159.1	154.1	415.0	317.7	1105.0	
420	3469.1	1789.7	216.5	164.5	505.3	361.1	928.0	N/A
420	2362.1	1259.5	152.7	119.9	363.9	261.1	1005.5	
420	3464.7	1896.2	232.6	192.7	554.2	369.2	1026.2	
Mean Concentrations								
1	4753.3	2754.7	361.5	357.0	869.1	562.1	971.2	
7	4160.8	2316.7	286.5	276.1	694.5	473.8	1042.6	
21	3481.5	2020.1	255.6	257.0	655.7	438.4	1001.9	
49	4295.8	2404.9	315.7	291.5	737.1	490.6	1033.2	
120	2710.9	1492.6	189.5	176.9	463.2	315.6	1097.9	
232	3289.9	1620.3	183.4	162.4	434.8	320.6	1118.9	
280	2167.6	1179.2	141.2	131.1	352.2	259.6	1089.2	
420	3098.6	1648.4	200.6	159.0	474.5	330.5	986.6	

15% MTBE AND PS-6 GASOLINE

DAY	B	T	E	P-XYL	M-XYL	O-XYL	MTBE	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L
Active Microcosms								
1	4869.4	2785.3	361.0	358.3	877.5	578.0	311.7	6.1
1	4762.7	2711.1	350.7	349.3	854.1	562.7	311.0	
1	4789.5	2725.6	352.4	347.9	856.1	562.3	322.4	
7	4418.7	2525.7	314.0	300.0	752.7	514.3	343.0	1.0
7	4443.1	2358.8	256.1	188.4	286.6	365.6	337.8	
7	3910.4	1900.5	223.8	161.3	253.2	344.3	355.4	
21	3819.6	1797.4	210.5	143.9	217.0	331.7	292.3	<DL
21	3925.9	1842.4	224.8	157.4	243.7	365.8	296.4	
21	3924.4	1910.7	238.0	166.3	254.3	375.2	293.1	
49	4045.8	1976.1	205.9	90.4	76.5	244.7	359.1	<DL
49	4155.0	1840.7	168.3	49.8	25.9	143.3	345.4	
49	4030.1	2028.4	224.2	109.3	106.3	275.8	351.2	
120	3777.9	1857.4	2.2	218.8	129.8	184.4	347.1	<DL
120	3800.4	1664.8	213.9	142.3	238.1	351.8	372.9	
120	3686.2	1804.6	205.9	119.9	173.0	312.5	362.7	
232	4105.9	1729.5	187.4	111.4	214.3	297.1	365.9	<DL
232	4103.9	1815.9	164.0	78.8	87.6	220.1	359.3	
232	4008.2	1682.8	193.7	118.2	206.5	296.4	318.6	
280	3755.0	1654.9	197.0	116.9	217.5	305.9	372.8	<DL
280	3592.5	1646.9	206.0	130.7	242.8	324.8	358.8	
280	3432.8	1530.8	189.1	125.3	248.6	315.1	347.1	
420	3471.3	1588.3	149.3	51.0	45.8	198.3	21.1	<DL
420	3283.2	1457.6	174.9	106.3	238.8	298.4	166.6	
420	2866.5	1260.2	145.6	82.0	208.6	264.7	8.6	

DAY	B	T	E	P-XYL	M-XYL	O-XYL	MTBE	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L
Mean Concentrations								
1	4807.2	2740.6	354.7	351.8	862.6	567.7	315.0	6.1
7	4257.4	2261.6	264.6	216.5	430.8	408.1	345.4	1.0
21	3889.9	1850.2	224.4	155.9	238.3	357.6	293.9	<DL
49	4077.0	1948.4	199.5	83.2	69.6	221.2	351.9	<DL
120	3754.8	1775.6	140.7	160.3	180.3	282.9	360.9	<DL
232	4072.7	1742.8	181.7	102.8	169.5	271.2	347.9	<DL
280	3593.4	1610.9	197.3	124.3	236.3	315.3	359.6	<DL
420	3207.0	1435.3	156.6	79.8	164.4	253.8	65.4	<DL
Control Microcosms								
1	4549.7	2589.2	336.1	332.3	814.5	533.5	297.7	N/A
1	4613.8	2637.8	345.0	342.1	827.9	549.7	315.1	
1	4747.0	2716.6	353.1	353.6	874.6	562.4	318.1	
7	3926.8	2331.1	297.6	289.8	729.6	498.0	355.0	N/A
7	3928.8	2167.7	249.7	236.0	611.8	426.2	322.4	
7	4111.7	2355.6	289.9	277.8	706.5	477.3	345.1	
21	690.3	437.6	52.7	56.2	151.1	134.2	232.5	N/A
21	111.1	63.1	27.2	12.2	20.5	21.2	148.7	
21	4000.4	2307.9	287.1	289.5	729.7	480.7	290.2	
49	2789.0	1642.4	223.1	202.8	524.8	382.7	339.6	N/A
49	3862.6	2187.4	284.7	262.5	662.3	460.8	338.3	
49	3874.8	2284.0	316.1	299.1	765.3	514.3	342.4	

DAY	B	T	E	P-XYL	M-XYL	O-XYL	MTBE	O_2
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	mg/L	mg/L
120	3669.7	2040.2	247.1	228.3	610.0	432.0	312.4	N/A
120	128.6	50.9	7.3	5.0	14.2	23.6	218.5	
120	2114.6	1268.0	160.0	153.4	415.8	322.9	324.4	
232	4080.7	2003.2	220.4	193.2	526.0	381.8	347.1	N/A
232	4036.6	1978.3	212.4	185.1	98.3	370.4	357.4	
232	3993.9	2044.3	228.0	205.3	544.8	386.0	318.9	
280	66.0	22.7	<DL	<DL	<DL	<DL	45.1	N/A
280	3959.9	2122.6	246.3	217.1	597.0	438.1	352.1	
280	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
420	3388.1	1763.4	218.3	158.9	477.6	356.1	1.4	N/A
420	61.2	23.9	<DL	<DL	<DL	<DL	15.6	
420	41.5	23.7	<DL	<DL	<DL	<DL	26.1	
Mean Concentrations								
1	4636.8	2647.9	344.7	342.7	839.0	548.5	310.3	6.1
7	3989.1	2284.8	279.1	267.9	682.7	467.2	340.8	1.0
21	1600.6	936.2	122.4	119.3	300.4	212.0	223.8	N/A
49	3508.8	2037.9	274.6	254.8	650.8	452.6	340.1	N/A
120	1971.0	1119.7	138.1	128.9	346.6	259.5	285.1	N/A
232	4037.1	2008.6	220.3	194.5	389.7	379.4	341.1	N/A
280	2673.2	1396.6	158.1	140.8	380.6	274.7	238.7	N/A
420	1163.6	603.6	72.8	53.0	159.2	118.7	14.4	N/A

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