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DELINEATION AND CHARACTERIZATION OF THE BORDEN MTBE PLUME: AN EVALUATION OF EIGHT YEARS OF NATURAL ATTENUATION PROCESSES

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Delineation and Characterization of the Borden MTBE Plume: An Evaluation of Eight Years of Natural Attenuation Processes

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4668

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The views expressed here are those of the authors.

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ABSTRACT

In 1988, a natural gradient tracer test was performed in the shallow sand aquifer at Canadian Forces Base (CFB) Borden. This study investigated the fate of a methyl-tertiary-butylether (MTBE) plume introduced into the Borden aquifer in order to quantify the status of this contaminant in shallow, aerobic settings. Solutions of groundwater mixed with oxygenated gasoline were injected below the water table along with chloride (Cl⁻), a conservative tracer. The migration of benzene, toluene, ethylbenzene, the xylenes (BTEX); MTBE; and CI was monitored in detail for about 16 months. The mass of BTEX compounds in the plume diminished significantly with time due to intrinsic aerobic biodegradation. MTBE, on the other hand, was not measurably attenuated. In 1995, additional exploratory sampling of the Cl and MTBE plumes found both at lower concentrations. The MTBE/CI ratio was more than two orders of magnitude lower than that of the injection solution and earlier sampling events suggesting some mass loss of MTBE may have occurred. In 1995-96, a comprehensive groundwater sampling program was undertaken to define the mass of MTBE still present in the aquifer. Since the plume had migrated into an unmonitored section of the Borden aquifer, numerical modeling and geostatistical methods were applied to find an optimal sampling grid. A drive-point profiling system was then used to obtain groundwater samples. In the 1995-96 sampling rounds, MTBE concentrations measured were more than an order of magnitude lower than expected based on the modeling that considered dispersion and diffusion as the only attenuation processes. A mass balance for the remaining MTBE mass in the aquifer eight years after injection was performed using the geostatistical software packages GEOSOFT™ and GMS[™]. Although the possibility exists that part of the MTBE plume was missed, the extensive sampling in a well-characterized aquifer, with the location of MTBE where it was anticipated, suggests otherwise. Only about 3 percent of the initial MTBE mass was found and it is hypothesized that biodegradation played an important role in the attenuation of the MTBE within the Borden aquifer. Nevertheless, additional lines of evidence of biodegradation, such as laboratory batch and column experiments, are necessary to confirm this possibility. Studies are underway, but no confirming laboratory evidence has been found to date. Thus, while there is confidence that MTBE mass has been lost, biodegradation cannot yet be confirmed as the process.

1-1

TABLE OF CONTENTS

| <u>Section</u> Page |
|--|
| EXECUTIVE SUMMARYES-1 |
| 1. INTRODUCTION |
| 2. THE MTBE FIELD EXPERIMENT AT CFB BORDEN, ONTARIO |
| 3. METHODS OF GROUNDWATER SAMPLING AND ANALYSIS |
| 4. SAMPLING STRATEGY FOR THE 1995-96 SAMPLING ROUNDS 4-1 |
| 5. THE 1996 SAMPLING RESULTS 5-1 |
| 5.1. MTBE 5-1 |
| 5.1.1 MTBE Coarse Grid Sampling Results 5-1 |
| 5.1.2 MTBE Fine Grid Sampling Results 5-2 |
| 5.1.3 Additional MTBE Sampling Results 5-5 |
| 5.2. TERT-BUTYL ALCOHOL (TBA) AND TERT-BUTYL FORMATE (TBF) 5-5 |
| 5.3. CHLORIDE |
| 5.4. BTEX 5-6 |
| 5.5. OXYGEN 5-7 |
| 5.6. SULFATE 5-9 |
| 5.7. AMMONIA 5-9 |
| 6. SUMMARY AND DISCUSSION |
| 7. FUTURE WORK |
| REFERENCES |
| Appendix A PRELIMINARY MODELING AND RESULTS OF THE 1995 SAMPLING ROUNDA-1 |
| Appendix B |
| TWO-DIMENSIONAL MODELING USING RANDOM HYDRAULIC CONDUCTIVITY FIELDS |
| Appendix C |
| DETERMINATION OF THE OPTIMAL GRID SPACING USING GEOSTATISTICAL METHODSC-1 |

LIST OF FIGURES

| Figure | | Page |
|--------|---|------|
| 2-1. | Plan view position of the MTBE plume (upper) and the chloride plume (lower) 476 days after injection. | 2-2 |
| 2-2. | Calculation of depth integrated concentrations using vertically distributed concentrations at a single sampling location. | 2-4 |
| 2-3. | Mass of MTBE and Cl ⁻ in the MTBE slug over the initial 476 days of snapshot monitoring. | 2-5 |
| 2-4. | Mass of selected BTEX compounds in the MTBE slug over the initial 476 days of snapshot monitoring | 2-6 |
| 2-5. | Corrected mass of MTBE and Cl ⁻ in the MTBE slug over the initial 476 days of snapshot monitoring | 2-6 |
| 4-1. | Cross section of the Borden field site with the injection area (source), the last sampling snapshot at 476 days and the anticipated plume location 7 years after injection. | 4-2 |
| 4-2. | MTBE sampling results from the November 1995 sampling round with peak concentrations at each location in $\mu g/L$ | 4-3 |
| 4-3. | Location of a conservative MTBE plume 2920 days after injection, based on modeling three separate realizations using Borden aquifer hydraulic properties | 4-4 |
| 4-4. | The anticipated MTBE plume 2920 days after injection with depth integrated concentrations in mg/m^2 . | 4-5 |
| 4-5. | Sampling locations for the coarse grid sampling round in 1996 | 4-7 |
| 5-1. | Sampling locations with depth integrated MTBE concentrations (mg/m ²) for the coarse grid sampling round. | 5-2 |
| 5-2. | Sampling locations with depth integrated MTBE concentrations (mg/m ²) for the fine grid sampling round | 5-3 |
| 5-3. | Additional bundle piezometers installed along transect A - A' at locations B, C and D. | 5-4 |
| 5-4. | Examples of MTBE depth profiles for the transect A - A' | 5-4 |

LIST OF FIGURES (Continued)

| <u>Figure</u> | | Page |
|---------------|--|------|
| 5-5. | Sampling locations with depth integrated total BTEX concentrations (mg/m^2) for the fine grid sampling round | 5-7 |
| 5-6. | Dissolved oxygen concentrations (mg/L) at various depths at locations B, C and D using bundle piezometers. | 5-8 |
| 5-7. | Examples of MTBE / Sulfate depth profiles for the transect A - A'. | 5-9 |
| 5-8. | Sampling locations with depth integrated ammonia concentrations (g/m^2) for the fine grid sampling round. | 5-10 |
| 6-1. | Schematic cross section of the vertical MTBE concentration distribution from injection until 1996 | 6-2 |
| 6-2. | Depth integrated and time corrected MTBE concentrations (mg/m ²) for all sampling rounds. | 6-3 |
| 6-3. | MTBE field mass estimates with the initial sampling rounds (up to 476 days) and the final sampling round about 8 years (3000 days) after injection | 6-7 |

LIST OF TABLES

| <u>Table</u> | | Page |
|--------------|--|------|
| 2-1. | Mass and concentration of solutes initially injected and mass determined by snapshot sampling at later times. | 2-3 |
| 4-1. | Minimum mass recovered from a simulated MTBE plume using different sampling grid designs | 4-7 |

EXECUTIVE SUMMARY

SUMMARY

This study investigates the fate of a methyl tertiary-butyl ether (MTBE) plume eight years after it was introduced into a shallow water table aquifer to evaluate and quantify natural attenuation processes. The objective of the study was to characterize the total remaining mass of MTBE and its distribution in the aquifer. Numerical and analytical models and geostatistical methods were used to design optimal sampling grids for several sequential field sampling events. These same techniques were used to interpret and analyze the field results to identify the primary mass loss mechanisms affecting the fate and transport of MTBE in this aquifer over the eight year period following the initial injection. The results of this analysis suggest that biodegradation processes are the most likely mass loss mechanism affecting MTBE transport in the Borden aquifer.

BACKGROUND

MTBE was first blended in gasoline in 1979 to replace lead and to increase octane. Its use has increased rapidly over the last decade. In 1988 the first wintertime oxygenated fuel (oxyfuel) program was implemented in Denver using gasolines with 15% MTBE (by volume) to reduce vehicle carbon monoxide emissions. Wintertime oxyfuel programs began in 30 other non-attainment areas in 1992-93. Reformulated gasoline (RFG) has 11% MTBE by volume and was introduced in ozone non-attainment areas in 1995.

Natural attenuation is an increasingly utilized corrective action technology at motor fuel release sites with groundwater contamination. A recent evaluation of benzene plume characteristics at underground storage tank (UST) sites in California concluded that natural attenuation processes such as sorption, dispersion and biodegradation limit the size and impacts of such plumes, and recommended that "passive" or "intrinsic" bioremediation be considered



the primary remediation alternative at UST sites whenever possible (Rice *et al.*, 1995). Intrinsic bioremediation of gasoline-contaminated groundwater relies on biodegradation of benzene, toluene, ethylbenzene and the xylene isomers (BTEX) by naturally occurring microorganisms to achieve remedial objectives.

MTBE has somewhat distinctive physical and chemical properties relative to other gasoline components. It has a water solubility of about 50,000 mg/L and is therefore more than 25 times more soluble than benzene. Its organic carbon-based partition coefficient (K_{OC}) is 11 cm³/g, about 10 times less than benzene, which results in minimal sorption and retardation in natural aquifers. MTBE has a moderate dimensionless Henry's law Constant (concentration in air/concentration in water) of about 0.04 at 25 °C (almost 10 times less than benzene, meaning it is less likely to volatilize from water, either naturally or during active air stripping). Finally, MTBE has a very strong taste and odor and so may impair drinking water quality at aqueous concentrations as low as 20 - 40 μ g/L (USEPA, 1997).

The biodegradability of MTBE appears to differ from that of the BTEX compounds. The presence of both an ether bond and a tertiary carbon group within the structure of MTBE (i.e., it is a branched alkyl ether) suggests it will be more resistant to degradation by microbial populations than most petroleum hydrocarbons. While early studies indicated that MTBE is usually non-biodegradable in groundwater (e.g., Suflita and Mormile, 1993; Novak *et al.*, 1985), recent work has provided increasing evidence of at least limited biodegradability. Salanitro *et al.* (1994, 1996) isolated a bacterial culture that could degrade MTBE under laboratory conditions. In addition, Borden and co-workers found evidence of MTBE biodegradation at a field site in North Carolina combining information obtained by laboratory batch experiments and field monitoring (Borden *et al.*, 1997).

As near-source concentrations of MTBE may exceed 10,000 - 20,000 μ g/L, reliance on dispersive attenuation processes alone may be insufficient to provide adequate protection to down-gradient receptors. As a result, the occurrence of MTBE in gasoline-impacted

groundwater may sometimes limit the use of intrinsic remediation because MTBE is more mobile and more persistent than BTEX in shallow, aerobic aquifers. Compared to BTEX, very little field information is available to provide reliable estimates of its natural attenuation, or the factors that may influence its rate of natural attenuation at specific sites. The study described in this report is intended to provide a better understanding of the behavior of MTBE in groundwater, especially the role of biodegradation.

THE INITIAL INJECTION OF MTBE

In 1988 and 1989, a natural gradient tracer test was performed in the shallow, aerobic sand aquifer at Canadian Forces Base (CFB) Borden in Ontario, Canada. A key objective of that study was to evaluate the fate and transport of MTBE and BTEX compounds. About 2800 liters of groundwater, spiked with Cl⁻ (448 mg/L), gasoline-derived organics (including about 19 mg/L BTEX) and MTBE (269 mg/L), were injected 1.5 m below the water table. This mixture created a discrete slug of MTBE-contaminated groundwater traveling at a velocity of about 33 m/year under natural gradient conditions. Separate, adjacent dissolved plumes were also injected at that time representing releases from non-oxygenated gasoline and from a methanol/gasoline mixture.

The migration of the contaminants was monitored by detailed groundwater sampling using a dense network of multilevel piezometers, typically using 14 depth-points over a 2.8 -4.2 m vertical zone. These sampling snapshots of contaminant distribution were obtained 6, 42, 106, 317, 398, and 476 days after injection. The BTEX compounds underwent rapid aerobic biodegradation and were almost completely attenuated during the initial 16 month period. The experiment and the fate of the monitored compounds are discussed in detail by Hubbard *et al.* (1994).

Based on the total mass present, the mass ratio MTBE/CI⁻ was about 0.59 initially and remained about the same until day 476 when it had decreased to 0.43. The MTBE/CI⁻ concentration ratios for single samples ranged from 0.33 to 1.0 for the initial 476 days of the experiment. Due to the uncertainty of the field mass balance estimates, degradation of MTBE

could not be demonstrated and it was concluded at the time that the compound was either persistent over the 16 months of monitoring or degrading at a rate not detectable under the experimental conditions (Hubbard *et al.*, 1994).

THE MTBE PLUME EIGHT YEARS LATER

No additional monitoring of the injected MTBE plume had occurred subsequent to the final round of sampling for the original study in 1989. In late 1995, in response to increased interest in the long-term behavior of MTBE in groundwater, a comprehensive sampling program was undertaken to locate and define the mass of MTBE still remaining in the aquifer. Three major sampling events were planned and designed with the use of both analytical and numerical flow/transport models as well as with statistical analyses. The main goal was to delineate the MTBE plume in enough detail to perform a reliable mass balance and to compare the remaining MTBE mass in the aquifer with the amount originally injected.

The physical properties, hydraulics and geochemistry of the Borden aquifer have been exceptionally well characterized. The aquifer is relatively homogeneous and the statistical properties describing the hydraulic conductivity field are well defined. The aquifer lies over an extensive regional clayey and sandy silt aquitard that is approximately 8 m thick at the field site. The mean groundwater velocity in the aquifer is about 33 m/year and the northwards flow direction fluctuates seasonally about 20 degrees. The Borden aquifer has a relatively low carbon content of 0.02 percent and thus a low sorption capacity for organic compounds.

The analytical and numerical models used to characterize flow and transport predicted that by the end of 1995, the MTBE plume should have migrated 240 m beyond the injection location and about 200 m beyond the last sampling snapshot taken at 476 days. Given that the plume had traveled well beyond the 1988/89 sampling grid, no network of multilevel sampling devices was available for sampling. Rather than install a new multi-level piezometer network, the Waterloo drive-point profiler was used to collect multiple groundwater samples at various

STD.API/PETRO PUBL 4668-ENGL 1998 📰 0732290 0611372 147 📰

depths at a number of locations. With this direct-push system, a stainless steel sampling device is driven downward by pressure and vibration. De-ionized water is constantly injected to keep the sampling ports of the drive-point piezometer open and to avoid cross-contamination. Samples are collected at desired depths through stainless steel or Teflon[®] tubing connected through the drive rods to a peristaltic pump.

Three sampling rounds were carried out (November 1995; July/August 1996; November 1996). Samples obtained in the first sampling round were analyzed for MTBE at a commercial laboratory using EPA's SW-846 GC/MS Method 8240. Beginning in 1996, samples were analyzed at the Oregon Graduate Institute using a direct aqueous injection (DAI) GC/MS technique to determine MTBE, tert-butyl alcohol (TBA) and tert-butyl formate (TBF) (Church *et al.*, 1997). With this method, very low detection limits were obtained: 0.1, 0.1 and 10 μ g/L for MTBE, TBA and TBF, respectively.

RESULTS

The field sampling was successful in locating an MTBE plume at a location that, considering all the uncertainty involved in modeling such a long-term experiment, was in good agreement with the location suggested by numerical modeling. Generally, non-detect levels of MTBE were found at the peripheries of the sampling grid suggesting that the full lateral extent of the plume was delineated. The detection limits for MTBE in this study were very low (0.1 μ g/L), which would indicate that it is unlikely that much MTBE mass would be present outside the periphery of the identified plume. The highest MTBE concentrations, however, were more than an order of magnitude lower than expected based on numerical modeling that considered dispersion and diffusion as the only attenuation mechanisms. Numerical modeling with no consideration of degradation predicted maximum concentrations in excess of 3000 μ g/L; field sampling found maximum concentrations of less than 200 μ g/L. Further, using the field sampling results to calculate the remaining MTBE mass in the aquifer eight years after injection showed that only 3 percent of the original mass remained.

ES-5

MTBE/Cl⁻ concentration ratios were calculated for each sampling point and found to be between 0.001 and 0.008, much lower than the ratios of 0.33 to 1.0 calculated during the initial 16 months of the experiment. This drop in the MTBE/Cl⁻ ratio could either suggest that MTBE had undergone transformation or that additional Cl⁻ from other sources, such as the underlying landfill leachate plume, had mixed with the plume. Neither TBA nor TBF, two potential MTBE degradation products, was found in any of the samples. This could suggest that MTBE had not been transformed or that these compounds are also degraded readily if they are formed. Finding potential degradation products is usually a good indication of transformation; however, in the case of very slow degradation rates, as expected for MTBE, those compounds might be found at concentrations too small to be measured.

This mass balance comparison of predicted versus observed MTBE mass suggests a significant loss of MTBE in the Borden aquifer, which could potentially be attributed to biodegradation, abiotic degradation, sorption, volatilization, or plant uptake. Abiotic MTBE degradation involving subsurface material was only shown in one set of experiments by Yeh and Novak (1995). These researchers found MTBE to hydrolyze when hydrogen peroxide was added but iron was needed to act as a catalyst. This reaction is not favored in aerobic or near-neutral (pH > 6.5) environments such as the Borden aquifer and therefore is not likely to contribute to MTBE mass loss in this study. Based on linear sorption, the calculated MTBE retardation factor is 1.02 for the Borden aquifer (Schirmer *et al.*, 1998). This low value suggests that sorption cannot account for the large discrepancy between the initial and final MTBE mass. Furthermore, the MTBE was introduced into the aquifer 1.5 m below the water table; therefore, volatilization is not an attenuation factor in this experiment.

Plant uptake or phytoremediation is another potential attenuation factor. At the site, two forested areas exist with predominantly aspen and pine trees and ferns. The main orientation of tree roots is horizontal, not vertical, and such roots generally spread horizontally as far as 1-3 times the tree height. Almost 90 percent of a tree's roots can be found within the upper 0.6 m of soil (Dobson and Moffat, 1995). Root growth has been found to stop completely when air space dropped to 2 percent. Thus, at the Borden field site, where the top of the capillary fringe is found

ES-6

2 - 3 m below ground, it is doubtful that vertical root penetration extends beyond this depth and reaches the water table. For these reasons it is very unlikely that plant uptake influenced the MTBE plume introduced 1.5 m below the water table.

Although the possibility exists that a part of the remaining MTBE plume was missed by the sampling effort described here, it is believed that this is an unlikely outcome given 1) the extensive sampling in a well-characterized aquifer, 2) the clearly defined perimeter of the plume, 3) the very low analytical detection limits used to identify the plume perimeter, and 4) the location of MTBE where it was anticipated to be from the modeling results.

Given that only about 3 percent of the initial MTBE mass was found, and the apparent lack of other mechanisms that may account for the mass loss, it is hypothesized that biodegradation played an important role in the attenuation of the MTBE within the Borden aquifer. However, the design of this study could not provide direct evidence of such microbiological attenuation. It is, however, interesting to note that MTBE was present only in the deepest portion of the aquifer, close to the underlying aquitard. Previous studies at this site have indicated that the bottom part of the Borden aquifer may be impacted by a dilute, anaerobic landfill leachate plume. If this zone does exert its geochemical influence here, the persistence of MTBE in this part of the aquifer suggests MTBE has mixed with this anaerobic zone where it would be less susceptible to biodegradation. Results of other studies have shown that MTBE is more biodegradable in aerobic environments than in anaerobic environments.

Additional lines of evidence such as batch and column laboratory experiments using Borden aquifer materials are necessary to help confirm the amount of MTBE mass loss observed in this study that is attributable to biodegradation. Such studies are underway, but no confirmatory laboratory evidence has been found to date. Thus, while there is much confidence that MTBE mass has been lost from the Borden aquifer plume, it is not yet possible to confirm biodegradation as the process.

ES-7

REEXAMINATION OF THE 1988-89 STUDY DATA

The interpretation of major MTBE mass loss after 3000 days seems to contradict the suggestion of conservative behavior reported during the initial 476 days of transport (Hubbard *et al.*, 1994). These data were reexamined to characterize the trend in the recovered mass in the aquifer over the first 16 months following the injection. A regression analysis was performed on the MTBE mass calculations of that period, and interpretation of the results suggests that there was a small but statistically significant MTBE mass loss during the first 476 days of monitoring in 1988-89. Although the present study suggests that biodegradation was the main attenuation factor for MTBE in the Borden aquifer, it should be noted that this regression analysis represents only an apparent field mass loss rate and not necessarily a true rate of biodegradation.

CONCLUSIONS

This study provides field evidence of MTBE mass loss from a dissolved plume during the eight years subsequent to the original injection. Numerical modeling with no consideration of degradation predicted maximum concentrations in excess of 3000 μ g/L; field sampling found maximum concentrations of less than 200 μ g/L. A mass balance for the remaining MTBE mass in the aquifer eight years after injection showed that only 3 percent of the original mass remained. Consideration of all possible mass loss mechanisms leads to the suggestion that much of the MTBE within the Borden aquifer was biodegraded over a 3000 day period, a result somewhat contrary to the prevailing paradigm of MTBE resistance to biodegradation. Research is now needed to determine which types of subsurface environments do support MTBE biodegradation, and to define the microbiological and geochemical factors which influence MTBE biodegradation rates *in situ*. This understanding is necessary before biodegradation can routinely be considered as an attenuation mechanism for intrinsic remediation of MTBE in groundwater.

ES-8

Section 1 INTRODUCTION

Natural attenuation or intrinsic bioremediation is now widely promoted in North America and Europe as a possible solution to groundwater contamination. As of March 1996, 33 states in the US had endorsed intrinsic bioremediation as a viable corrective action approach at petroleum release sites. In California, Lawrence Livermore National Laboratories recommended that passive bioremediation be considered the primary remediation alternative at leaking fuel tank sites whenever possible (Rice *et al.*, 1995).

Intrinsic bioremediation of gasoline-contaminated groundwater generally relies on aerobic biodegradation of benzene, toluene, ethylbenzene and the xylene isomers (as a group termed BTEX) to achieve the desired concentration reductions. The occurrence of methyl-tertiary-butyl-ether [MTBE, $(CH_3)_3C(OCH_3)$] in gasoline contaminated groundwater may compromise the use of intrinsic bioremediation because MTBE is more mobile and apparently more persistent than BTEX in shallow aerobic aquifers.

MTBE is the most commonly used fuel oxygenate, added to gasoline primarily to increase octane and to reduce vehicle emissions. It appeared in gasoline in the Eastern United States in the early 1980s and in the Western States in the late 1980s (Squillace *et al.*, 1996 and Zogorski *et al.*, 1997). It was documented in groundwater contaminated by fuel leaks/spills as early as 1980 (McKinnon and Dyksen, 1984).

MTBE has very strong odor and taste and is likely to impair drinking water quality at aqueous concentrations of 15 - 75 μ g/L. Its environmental properties are compiled by Zogorski *et al.* (1997) and Squillace *et al.* (1997). MTBE is water soluble (50,000 mg/L) and therefore mobile in groundwaters. The organic carbon-based partition coefficient (K_{OC}) is 11 cm³/g which results in a very low sorption in natural aquifers. MTBE has a moderate dimensionless Henry's law constant (concentration in air in mg/L / concentration in water in mg/L) of 0.04 and therefore can be stripped from water in conventional air strippers, but requires a greater air flow than does

1-1

stripping of BTEX. The structure of MTBE with its strong ether bond suggests its resistance to biodegradation. Thus, MTBE is usually considered recalcitrant to biodegradation in groundwaters (e.g., Suflita and Mormile, 1993; Novak *et al.*, 1985), although Salanitro *et al.* (1994) isolated a bacterial culture that could degrade MTBE under laboratory conditions. Additionally, Borden and co-workers found evidence of MTBE biodegradation by combining information from laboratory batch experiments and field monitoring from a site in North Carolina (Borden *et al.*, 1997).

MTBE possesses many of the attributes of a difficult groundwater contaminant. Its likely high near-source concentrations (> 10 - 20 mg/L), low sorption, and the apparent lack of biodegradation in groundwater will make it more difficult to attain the large attenuation required to protect water well users (concentrations of < 15 μ g/L, the taste and odor threshold) by intrinsic bioremediation.

This study investigates the fate of an MTBE plume introduced into the Canadian Forces Base (CFB) Borden aquifer about eight years ago in order to characterize and quantify the status of this contaminant in shallow, aerobic aquifers. In 1988, about 2800 L of groundwater, spiked with chloride (448 mg/L), gasoline-derived organics (including about 19 mg/L BTEX) and MTBE (269 mg/L) were injected 1.5 meters below the water table into the shallow sand aquifer at CFB Borden. The migration of contaminants and chloride was monitored in detail for about 16 months. The mass of BTEX compounds in the plume diminished significantly with time due to intrinsic aerobic biodegradation. MTBE mass transport was similar to the chloride tracer and little or no decrease of the MTBE mass was observed. Due to the uncertainty of field mass balance estimates, it was concluded that the MTBE remained recalcitrant over the 16 months of monitoring (Hubbard *et al.*, 1994).

No further monitoring of this plume occurred until November 1995. In 1995, additional exploratory sampling of the chloride (Cl⁻) and MTBE plumes, now about 240 m downgradient of the injection area, found both to be at lower concentrations. The MTBE/Cl⁻ ratio had decreased by up to two orders of magnitude from the level in the injection solution and at earlier sampling

STD.API/PETRO PUBL 4668-ENGL 1998 📟 0732290 0611378 665 📟

events. This finding suggests that mass loss of MTBE may have occurred, perhaps due to biodegradation.

An extensive groundwater sampling program was undertaken in 1996 to define the mass of MTBE still present in the aquifer. A drive-point profiling system, the Waterloo Profiler (Pitkin *et al.*, 1994), was used to obtain groundwater samples. In the 1995/96 sampling rounds, MTBE concentrations of less than 200 μ g/L have been found, when concentrations far above 1000 μ g/L were expected if MTBE were recalcitrant. No tert-butyl alcohol (TBA) or tert-butyl formate (TBF), two potential degradation products of MTBE, has been found.

It is extremely difficult to conclusively quantify the different attenuation processes contaminants undergo within real aquifers (Madsen, 1991). Therefore, the suggestion that MTBE biodegradation has occurred within the eight years of travel time through the Borden aquifer has to be supported by additional lines of evidence. Currently, laboratory batch biodegradation experiments are planned to evaluate the suggestion that the MTBE mass loss observed in this field experiment was the result of natural biodegradation.

1-3

Section 2 THE MTBE FIELD EXPERIMENT AT CFB BORDEN, ONTARIO

In 1988, about 2800 L of groundwater, spiked with chloride (448 mg/L), gasoline-derived organics (including about 19 mg/L BTEX), and MTBE (269 mg/L) were injected 1.5 m below the water table into the shallow sand aquifer at CFB Borden. Two additional plumes were created by similarly introducing 2800 L of groundwater that had contacted gasoline alone and an additional 2800 L of groundwater that had about 7000 mg/L methanol added. These three additions created short-term slugs of contaminated groundwater that then moved downgradient at about 9 cm/day through the Borden sand aquifer under natural gradient conditions. This controlled field experiment is discussed in detail by Hubbard *et al.* (1994). The Borden aquifer is extremely well characterized in terms of its physical properties, hydraulics and geochemistry (e.g., Nicholson *et al.*, 1983; Mackay *et al.*, 1986; Frind and Hokkanen, 1987; Woodbury and Sudicky, 1991; Robin *et al.*, 1993; Schirmer *et al.*, 1995).

The progress of the contaminants was followed by detailed groundwater sampling using a dense network of multi-level (14 points) piezometers typically over a 4 m vertical zone which encompassed the three-dimensional extent of the dissolved plumes. These "snapshots" of contaminant distribution were obtained 6, 42, 106, 317, 398, and 476 days after injection. Subsequently, reconnaissance sampling has been conducted to locate and characterize the residual MTBE plume. This occurred in 1995 and 1996, from 2700 days to about 3000 days since the natural gradient experiment started. Figure 2-1 shows, in plan view, the positions of the chloride and MTBE plumes at day 476. The lack of retardation of the MTBE is evident in comparison to the chloride. All concentrations are presented as vertically integrated concentrations (Figure 2-2). Vertically integrated concentrations help to present complex three-dimensional concentration distributions in a two-dimensional plane. Integration of vertical concentration data using trapezoidal quadrature for equal spacing is obtained by the following equation:

$$C_{\text{integr}} = \Delta z/2 \ (c_1 + c_n + 2\Sigma c_i) \tag{2-1}$$

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| where | $\mathrm{C}_{\mathrm{integr}}$ | = | depth integrated concentration (ML ⁻²), |
|-------|--------------------------------|---|--|
| | Δz | = | distance between sampling points (L), |
| | c ₁ | = | solute concentration at top point (ML ⁻³), |
| | c _n | = | solute concentration at bottom point (ML ⁻³), |
| | $\mathbf{c}_{\mathbf{i}}$ | = | solute concentration at intermediary points (ML ⁻³). |
| | | | |

In the annotations, M refers to mass and L represents a length unit. The resulting vertically integrated concentrations have units of mg/L times meters (g/m³ times meters) which is equal to g/m^2 , or $\mu g/L$ times meters (mg/m³ times meters) which is equal to mg/m², respectively.



Figure 2-1. Plan view position of the MTBE plume (upper) and the Cl⁻ plume (lower) 476 days after injection. Contours are vertically integrated concentrations. For Cl⁻, contours are 10, 20, and 50 g/m², while MTBE contours are 1, 20, and 50 g/m².

2-2

Table 2-1 presents the initial concentrations and masses of chemicals introduced in the MTBE slug and the total mass of solute present at each snapshot. The initial masses of all constituents were recalculated from the original input concentration data and therefore, differ slightly from the initial masses reported (Hubbard *et al.*, 1994). The initial mass ratio MTBE/CI⁻, based on the total mass present, is about 0.59, and it remains about the same until day 476 when it was 0.43. Figures 2-3 and 2-4 show the changing mass of CI⁻, MTBE, benzene, toluene and o-xylene in the MTBE slug over the initial 476 days. Each mass includes the sorbed phase mass, with this total mass calculated as:

Total mass = Mass in solution x Retardation factor
$$(2-2)$$

This retardation factor was taken as 1 for MTBE, but ranged from 1.1 for benzene to 1.6 for p-xylene (Hubbard *et al.*, 1994).

| 1 | | | | | | | | |
|--------------|----------------------------|----------|----------|-----------|------------------------|------------|------------|------------|
| | Initial Conc. (mg/L) | Day 0 | Day 6 | Day 42 | Mass (g) Day 106 | Day 317 | Day 398 | Day 476 |
| Chloride | 448 | 1271 | 1410 | 1130 | 1150 | 780 | 650 | 1390 |
| Benzene | 7.7 | 22 | 22 | 23 | 16 | 10 | 6.4 | 5.5 |
| Toluene | 5.4 | 15 | 14 | 17 | 8.1 | 1.4 | 0.8 | 0.2 |
| Ethylbenzene | 1.0 | 2.7 | 2.5 | 2.5 | 1.8 | 0.7 | 0.3 | 0.08 |
| p-Xylene | 1.0 | 2.7 | 2.5 | 2.9 | 1.9 | 0.8 | 0.3 | 0.2 |
| m-Xylene | 2.5 | 7.0 | 6.7 | 6.7 | 2.9 | 0.3 | 0.2 | 0.0 |
| o-Xylene | 1.4 | 3.9 | 3.6 | 4.2 | 2.9 | 1.0 | 0.6 | 0.3 |
| MTBE | 269 | 752 | 700 | 700 | 670 | 360 | 340 | 600 |

Table 2-1. Mass and concentration of solutes initially injected and mass determined by snapshot sampling at later times.

2-3



Aquitard

Figure 2-2. Calculation of depth integrated concentrations using vertically distributed concentrations at a single sampling location. An example calculation using Equation 2-1 with $c_1 = 5 \text{ mg/L}$, $c_2 = 10 \text{ mg/L}$, $c_3 = 12 \text{ mg/L}$, $c_4 = 14 \text{ mg/L}$, $c_5 = 3 \text{ mg/L}$ and $\Delta z = 1.5 \text{ m}$ would yield a depth integrated concentration C_{integr} of 60 g/m².

Since Cl⁻ is conservative, its mass should remain constant for each sampling snapshot. On days 317 and 398, the calculated mass is low (Hubbard *et al.*, 1994) indicating that for these times, the plume capture was incomplete. The reason for this incomplete capture was that the piezometers of the sampling network did not penetrate the entire part of the aquifer through which the plume was moving. Part of the plume traveled below the deepest sampling points and was therefore missed. Thus, the mass estimates are likely to suffer a negative bias for these sampling events. Furthermore, since the field sampling showed that MTBE occupies essentially the same aquifer volume as does the Cl⁻, missing some of the Cl⁻ plume probably causes a similar proportion of the MTBE plume to be missed. The Cl⁻ mass can therefore serve as a correction factor for the incomplete MTBE plume capture. The uncorrected mass curves of measured constituents are shown in Figures 2-3 and 2-4 and the corrected masses of Cl⁻ and MTBE are presented in Figure 2-5. Here the Cl⁻ mass has been recalculated to its original value of 1271 g. The correction ratio has then been applied to MTBE for each sampling event. BTEX is retarded and usually occupied

2-4

less of the missing Cl⁻ plume volume; therefore, the correction may cause an overestimation of the actual BTEX masses. A correction for BTEX was not attempted. Keeping the uncertainty of field mass estimates in mind, neither analysis of the MTBE mass data suggests significant loss of MTBE during the 476 days of monitoring. However, the clear case for BTEX mass loss is shown in Figure 2-4.



Figure 2-3. Mass of MTBE and Cl⁻ in the MTBE slug over the initial 476 days of snapshot monitoring.



Figure 2-4. Mass of selected BTEX compounds in the MTBE slug over the initial 476 days of snapshot monitoring.



Figure 2-5. Corrected mass of MTBE and Cl⁻ in the MTBE slug over the initial 476 days of snapshot monitoring (see text for correction procedure details).

Section 3 METHODS OF GROUNDWATER SAMPLING AND ANALYSIS

At the end of 1995, more than seven years after injection, the MTBE plume was estimated to have migrated 240 m beyond the injection location and about 200 m beyond the last sampling location at 476 days (Appendix A). Since the plume had traveled well beyond the 1988-89 sampling grid, no network of multi-level sampling devices was available for sampling. Rather than install a new multi-level piezometer network, the Waterloo Profiler (Pitkin *et al.*, 1994) was used to collect multiple groundwater samples at various depths at a number of locations. With this direct-push system, a stainless steel sampling device is driven downward by pressure and vibration. De-ionized water is constantly injected to keep the sampling ports of the drive-point piezometer open and to avoid cross-contamination. Samples are collected at desired depths through stainless steel or plastic tubing connected through the drive rods to a peristaltic pump. After flushing, the sample is collected in a hypovial before the water passes through the pump tubing. As many as four samples were collected at one location to a total depth of 10 m below ground surface (bgs) within a three-hour period.

The sampling procedure was to advance the drive point profiler until it was driven into the aquitard. Sampling within the aquitard was attempted but in each case did not yield any sample water. In those cases where the distance between the last sampling point within the aquifer and the top of the aquitard was more than half of the vertical spacing, the sampler was slowly retrieved until groundwater could be collected, presumably just above the aquitard.

During sampling, three sample tube volumes plus 300 mL of ground water were flushed through the hypovials before the sample was collected. The pumping rate was less than 100 mL/min. MTBE samples for the first sampling round were acidified using two drops of a 1:1 HCl solution, packed on ice and overnight express mailed to a commercial laboratory. Following the analytical method described by Church *et al.* (1997), no preservatives were added to the samples for all other sampling events.

3-1

Sampling at the existing multi-level piezometers during the last sampling round was accomplished by purging at least 2 L of groundwater before the sample was taken. The pumping rate during sample collection was less than 100 mL/min.

Three sampling rounds were carried out (November 1995; July/August 1996; November 1996). Samples obtained in the first sampling round were analyzed for MTBE at a commercial laboratory using EPA's SW-846 Method 8240. Beginning in 1996, samples were analyzed at the Oregon Graduate Institute using a direct aqueous injection (DAI) GC/MS technique to determine MTBE, TBA and TBF (Church *et al.* 1997). With this method, detection limits were 0.1, 0.1 and 10 µg/L for MTBE, TBA and TBF, respectively. During the first and second sampling rounds, Cl⁻ was analyzed at the University of Waterloo to a detection limit of about 1 mg/L. For the final sampling round, Cl⁻, sulfate and ammonia analyses were performed at a commercial laboratory with detection limits of 0.5 mg/L for chloride, 2.0 mg/L for sulfate and 0.1 mg/L. NH₃/N for ammonia. Ion chromatography was used to determine the chloride and sulfate concentrations. The ammonia samples were first preserved with sulfuric acid and analyzed by a colorimetric method using a TechniconTM TRAACS System. A CHEMETRICSTM field oxygen probe was used to measure dissolved oxygen (DO) at selected locations in the field with a detection limit of 0.1 mg/L.

Section 4 SAMPLING STRATEGY FOR THE 1995-96 SAMPLING ROUNDS

The Borden aquifer is extremely well characterized in terms of its physical properties, hydraulics and geochemistry. The aquifer is fairly homogeneous with known statistical properties of its moderate heterogeneity (Woodbury and Sudicky, 1991; Robin *et al.*, 1993). The mean groundwater velocity is between 8.5 and 9.5 cm/day (31 - 35 m/year) and the flow direction fluctuates seasonally over about 20° (Farrell *et al.*, 1994). Although the flow field shifts over the year, the mean groundwater flow direction was observed to be very stable towards the North (e.g., Mackay *et al.*, 1986; Frind and Hokkanen, 1987; Hubbard *et al.*, 1994). The Borden aquifer has a relatively low carbon content of 0.02% which precludes a large sorption capacity (Nicholson *et al.*, 1983).

Based on the well known aquifer properties and hydraulics, some simple modeling was performed using the analytical solution SLUG3D (Sudicky, 1985) to estimate the expected MTBE plume location within the Borden aquifer about seven years after injection. The modeling suggested MTBE peak concentrations of more than 3,000 μ g/L should be found and that the plume would have moved about 200 m beyond the highly monitored portion of the aquifer (Figure 4-1). Details about the modeling are provided in Appendix A. An initial round of sampling was planned to determine if any portion of the plume could be located. The plan was to obtain about 100 samples along three transects perpendicular to the groundwater flow direction with 24 sampling locations and 3 to 4 sampling depths. Unfortunately, the weather conditions in November 1995 only allowed sampling at 13 locations (Figure 4-2). MTBE was detected at six of these locations with concentrations up to a maximum of 190 μ g/L. No conclusion could be drawn regarding whether the center or the periphery of the plume had been encountered because only much lower concentrations were found than suggested by modeling results. Chloride (Cl) concentrations were also measured and ranged from 3 mg/L to 42 mg/L, whereas the Cl⁻ background concentration is expected to be about 2 mg/L. The MTBE/Cl⁻ ratio during the 1988-89 monitoring was between 0.33 - 1.0 for single samples as well as for the overall mass. During the November 1995 sampling event, this ratio was found to be between 0.005 and 0.008. This

4-1

drop in the MTBE/Cl⁻ ratio suggests that MTBE may have undergone mass loss, traveled at a slower velocity than the Cl⁻, or that additional Cl⁻ from other sources, such as the landfill leachate plume, was encountered.



Figure 4-1. Cross section of the Borden field site with the injection area (source), the last sampling snapshot at 476 days and the anticipated plume location 7 years after injection. Note that the plume moved out of the highly monitored portion of the aquifer after day 476 and reached a forested area of the site at the time of the 1995-96 sampling.

As a second step, two-dimensional (2D) numerical simulations of depth integrated concentrations were performed since it is currently computationally impossible to perform a 3D analysis for a 2920-day (8 year) simulation time. It is generally accepted that the transverse (both vertical and horizontal) dispersion of contaminants in natural aquifers is minimal (e.g., Sudicky, 1986; LeBlanc *et al.*, 1991; Adams and Gelhar, 1992). This observation was confirmed during the first 476 days of the experiment (Hubbard *et al.*, 1994) and in other Borden field tests (e.g., Freyberg, 1986; Farrell *et al.*, 1994). Based on this evidence, the additional vertical spreading of the MTBE plume after the last sampling snapshot in 1990 was expected to be minor. Therefore, it was felt that the 2D modeling approach, ignoring vertical dispersion, was adequate.

4-2



Figure 4-2. MTBE sampling results from the November 1995 sampling round with peak concentrations at each location in µg/L. The three plumes represent the predicted 1000 µg/L contour lines of MTBE for average groundwater velocities of 8.5 cm/day (31 m/year), 9.5 cm/day (34.5 m/year) and 10.5 cm/day (38 m/year), respectively, calculated using SLUG3D without degradation.

Further computer simulations were performed to design an appropriate monitoring network to reliably sample the MTBE plume. To achieve more realistic results, three 2D random hydraulic conductivity (K) fields were generated using identical statistical parameters for the Borden aquifer. The numerical code FGEN92 (Robin *et al.*, 1993) was applied to create the random K fields. The statistical parameters are given by Woodbury and Sudicky (1991). The numerical program WATFLOW-3D (Molson *et al.*, 1995) was used to generate the flow field based on the random K distribution. The mean groundwater velocity in all three cases was about 9 cm/day (33 m/year). The numerical model BIO3D (Frind *et al.*, 1989; Schirmer *et al.*, 1995) was used to simulate the transport of MTBE over the 2920-day period from injection to an anticipated sampling in the summer of 1996 (Figure 4-3). MTBE was assumed to be conservative. The three realizations give insight into the uncertainty of the location of the

4-3

remaining MTBE, even in this very well-studied and relatively homogeneous aquifer. However, the average longitudinal and horizontal extent of the plumes is predicted as 40 and 12 meters, respectively, for the 500 mg/m² contour line of depth integrated concentrations. A sampling grid with a smaller spacing than 40 meters in longitudinal and 12 meters in transverse direction should be sufficient to find the location of the remaining plume. Subsequent detailed sampling in the areas where MTBE was found will help to define the MTBE mass present. Details about the modeling are provided in Appendix B.



Figure 4-3. Location of a conservative MTBE plume 2920 days after injection, based on modeling three separate realizations using Borden aquifer hydraulic properties.

Three to four sampling depths (0.25 - 1.0 m vertical spacing) per sampling location were proposed to delineate the vertical extent of the plume during the initial coarse grid sampling (Figure 4-1). During the fine grid sampling, the vertical spacing was refined at selected locations to 0.25 m vertical distance.

The next task was to find an optimal sampling grid with a minimal number of sampling locations while assuring that the plume is adequately characterized. Dixon and Chiswell (1996) give an overview on aquatic monitoring program designs. The authors state that the monitoring design depends mainly on the information goal. The challenge in the present study was to delineate the plume in great enough detail so that a reliable MTBE mass could be calculated. It was decided to obtain the optimal grid spacing based on statistical methods. Using the numerical model BIO3D in a 2D mode, several simulations were performed applying different random

4-4

hydraulic conductivity fields as described above. For each run, the calculated concentration distribution at 476 days simulation time was compared to the field measurements of the last sampling snapshot (476 days after injection). The simulation which reproduced the field results best was then run to 2920 days simulation time to provide a realistic distribution of the expected MTBE plume in the summer 1996 (Figure 4-4). MTBE was handled as conservative in the numerical simulations and hence the model conserves the mass of MTBE within the modeled domain. This provides the opportunity to computationally recover the known mass of MTBE using different grid spacings. The best sampling network design would then be a network which recovers most (i.e., more than 80%) of the initial MTBE mass with the least monitoring locations.



Figure 4-4. The anticipated MTBE plume 2920 days after injection with depth integrated concentrations in mg/m². Contours are 3000, 1000, and 500 mg/m².

The KRIGING routine together with the GRIDVOL (grid volume) option of the geostatistical software package GEOSOFT[™] were used to determine the recovery of the known mass of MTBE for different grid spacings. It was decided to test three different grid spacings in transverse (5 m, 7.5 m, and 10 m) and longitudinal direction (10 m, 15 m, and 20 m),

respectively. Obviously, the smaller the grid spacing, the more sampling locations are needed to cover the entire MTBE plume. Although the Borden aquifer is very well characterized, there is some uncertainty with respect to flow direction and velocity. Therefore, it was decided to use a grid which covers a large enough area so that the plume is not missed in longitudinal or transverse direction. The corresponding number of imaginary sampling locations was therefore chosen as 30, 42, and 55 for a longitudinal spacing of 20 m, 15 m, and 10 m, respectively. Each generated grid was laid on top of the simulated plume and the simulated concentration was found for each imaginary sampling location. Then the KRIGING option was used to calculate the mass recovery. In addition, each single grid was then shifted over the domain of the simulated plume. The recovered mass was calculated for each shift to ensure that a reasonable mass recovery was not by chance. The lowest recovered mass for each grid spacing is reported as the worst case scenario.

Since the generated plume (Figure 4-4) is long and thin, the mass recovery is much more sensitive to the transverse spacing than to the longitudinal one. For large grid spacings, as expected, fewer sampling points are located within or close to the plume center, and so less mass is recovered. See Appendix C for details on the calculations. Table 4-1 shows the minimum mass recovered for each grid spacing, independent of the locations of the sampling points (e.g., at the center of mass or at any other location within an individual grid). A recovery of at least one-third (36%) of the plume mass is obtained for even the coarsest grid spacing of 20 m in longitudinal and 10 m in transverse direction.

Considering these calculations and the uncertainties in flow direction and average groundwater flow velocity, a reconnaissance sampling was conducted using a coarse grid covering a 100 m x 40 m area with 30 sampling locations spaced 20 m apart longitudinally and 10 m apart transversely (Figure 4-5). This spacing was considered sufficient to delineate the general extent of the plume. Four to eight sampling points were distributed vertically at each location. After reviewing the field results, a fine grid (sampling location spacing of 5 to 15 m) in the area of MTBE occurrence was designed to define the remaining mass of MTBE within the aquifer.

4-6

| Table 4-1. | Minimum ma | ss recovered from a | simulated MTBE | plume using | different sampling |
|------------|---------------|----------------------|-------------------|-------------|--------------------|
| | grid designs. | (For detailed explar | nation see text). | | |

| Longitudinal Spacing | | | | | |
|----------------------|------|------|------|--|--|
| Transverse Spacing | 20 m | 15 m | 10 m | | |
| 10 m | 36% | 38% | 44% | | |
| 7.5 m | 38% | 40% | 49% | | |
| 5 m | 61% | 63% | 81% | | |



Figure 4-5. Sampling locations for the coarse grid sampling round in 1996. A longitudinal spacing of 20 m and a transverse spacing of 10 m were chosen. The plume contour lines are 3000, 1000, and 500 mg/m² for the modeled plume.

In order to have confidence in the numerical simulations, it was important to assess whether the assumed statistical properties for the numerical flow and transport modeling hold for the entire aquifer. Therefore, after completion of the field sampling, soil cores were taken from

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the aquifer portion through which the plume had moved. Hydraulic conductivity (K) measurements were performed to investigate whether the aquifer properties in this portion of the aquifer are close to the properties used to calculated the statistics of the aquifer (Sudicky, 1986).

The K values were calculated using permeameter tests at subsections of three cores and ranged from 4.5 x 10^{-5} to 1.49 x 10^{-4} m/s with a mean value of 1.04 x 10^{-4} m/s which compares well to the values found by Sudicky (1986) [6 x $10^{-6} \le K \le 2 x 10^{-4}$ m/s; mean K = 9.75 x 10^{-5} m/s]. Based on these results, it is appropriate to assume the same statistical hydraulic parameters for the whole study area.

Furthermore, in order to adequately describe the hydraulics at the field site and to investigate the possibility of movement of large amounts of groundwater from the aquifer into the aquitard, the hydraulic properties of the aquitard were assessed. The aquifer with a mean K value of 9.75×10^{-5} m/s is underlain by a continuous, about 8 m thick, unweathered clayey till aquitard. Based on the hydraulic response to a 38 day pumping test, it was found that the aquitard does not have any significant vertical fractures (Foley, 1992). The aquitard itself overlies a semi-confined aquifer. The pressure head difference between the semi-confined aquifer and the upper aquifer is 3.5 m yielding a downwards flow component through the aquitard with a gradient of 3.5m / 8m = 0.4375. Nine consolidation tests were performed (Foley, 1992) to calculate K values for the aquitard ranging from 1.12×10^{-10} to 5.39×10^{-10} m/s. The mean K value (2.4×10^{-10} m/s) is close to the typical values of southern Ontario lacustrine clay and thus more than five orders of magnitude lower than the mean K value of the overlying aquifer (Foley, 1992). Based on Darcy's law and the mean K value of the aquitard, a Darcy flux through the aquitard of about 3.3 mm/year was calculated. This value clearly indicates that the flux from the aquifer into the aquitard is extremely small.

4-8
Section 5 THE 1996 SAMPLING RESULTS

5.1. MTBE

The 1996 sampling was separated into two major rounds, the coarse and the fine grid sampling. The coarse grid sampling was initiated to cover a large enough area to find the boundaries of the MTBE plume. The fine grid sampling served to delineate the plume in great enough detail to perform a mass balance between the remaining MTBE plume mass and the mass of MTBE originally injected. Additional sampling was performed to determine if there were shallow MTBE plume segments present in the aquifer that potentially moved faster or slower than the segment identified in the three main sampling rounds.

5.1.1 MTBE Coarse Grid Sampling Results

The coarse grid sampling was performed in July/August 1996. Figure 5-1 shows the grid and depth integrated MTBE concentrations obtained during this sampling round. Since MTBE is not used in gasoline in this part of Canada and no MTBE users are known at CFB Borden, the MTBE background concentration in the aquifer is expected to be zero. Therefore, all the MTBE found should come from original injection. The sampling locations were spaced 20 m longitudinally and 10 m transversely with respect to the groundwater flow direction. If the entire plume lies within the covered area, at least 36 percent of the plume mass should be recovered (see Table 4-1). The vertical spacing at the sampling locations was 0.25 - 1.0 m. Due to time constraints, one sampling transect (between the pine forests; see Figure 4-5) could not be completed. However, this area was sampled during the initial sampling round in November 1995 (Figure 4-4). Only 5 of the 21 locations sampled contained MTBE at concentrations above the detection limit of $0.1 \mu g/L$. These few MTBE hits did not allow a conclusion that the entire plume was encountered. There was the possibility that the plume might have moved beyond the sampling grid. The task of the fine grid sampling was therefore twofold. First, it had to assure

5-1

that the periphery of the plume had been defined, and second, that the sampling grid had to be refined in order to perform a meaningful mass balance.



Figure 5-1. Sampling locations with depth integrated MTBE concentrations (mg/m²) for the coarse grid sampling round. A longitudinal spacing of 20 m and a transverse spacing of 10 m were chosen.

5.1.2 MTBE Fine Grid Sampling Results

The fine grid sampling was carried out in November 1996. The first priority was to ensure that the entire plume was delineated (i.e., that it had not moved farther than the area covered by the coarse grid sampling round). To test this hypothesis, several locations were placed beyond the coarse sampling grid in the vicinity of the road (Figure 5-2). The northernmost and easternmost sampling locations did not show any MTBE, so it was concluded that the plume is within the previously sampled area. The sampling grid was then refined to

5-2

ensure a plume coverage that allowed the performance of a mass balance. The vertical spacing at the sampling locations was 0.25 - 0.75 m. Figure 5-2 shows the grid and depth integrated MTBE concentrations for the entire fine grid sampling round. Nine of the 25 locations sampled contained MTBE with a detection limit of $0.1 \mu g/L$. As during previous sampling rounds, MTBE was only found at the vertically deepest sampling points close to the aquitard. Figure 5-3 shows the location of representative sampling points (transect A-A'; locations B, C and D) and Figure 5-4 presents the actual vertical MTBE concentration distribution along transect A-A'. The mass balance calculations are discussed in the next section.



Figure 5-2. Sampling locations with depth integrated MTBE concentrations (mg/m²) for the fine grid sampling round. Stars indicate sampling locations where existing multi-level piezometers were sampled in depths of 0.3 - 3.5 m below the water table.



Figure 5-3. Additional bundle piezometers installed along transect A - A' at locations B, C and D.



Aquitard

Figure 5-4. Examples of MTBE depth profiles for the transect A - A'. MTBE concentrations are in $\mu g/L$, whereas "nd" indicates a concentration below the detection limit of 0.1 $\mu g/L$.

5-4

5.1.3 Additional MTBE Sampling Results

At the Borden field site, vertical splitting of injected slugs into faster and slower moving segments has been noted (e.g., Sudicky *et al.* 1983). In November 1996, additional sampling sought such a shallow MTBE slug, moving faster than the slug identified in the above sampling rounds. Twelve multi-level piezometers, located in the area north of the road (Figure 5-2), with sampling ports 0.3 - 3.5 m below the water table were sampled. Two samples at each piezometer were collected. There was no detection of MTBE in any of those samples. These data show that there is no fast moving MTBE slug with high MTBE concentrations in the upper portion of the aquifer.

In addition, sampling is still ongoing at three locations (B, C, and D in Figure 5-3) where new multi-level piezometers were installed. These piezometers penetrate a large part of the aquifer down to the aquitard, at a spacing of 25 cm. These piezometers are sampled on a bimonthly basis to detect a potentially slower moving plume with high MTBE concentrations. Until September 1997, ten months after the last major sampling round, no MTBE was detected in the upper part of the aquifer and only small MTBE concentrations of less than 30 μ g/L were found close to the aquitard, as expected from the previous sampling events. To date, these data show that there is no slow moving slug with high MTBE concentrations (Schirmer *et al.*, 1997).

5.2. TERT-BUTYL ALCOHOL (TBA) AND TERT-BUTYL FORMATE (TBF)

During the coarse and fine grid sampling, analyses for TBA or TBF, two potential degradation products of MTBE, were performed. No TBA or TBF has been found. The detection limits were 0.1 and 10 μ g/L, respectively.

5.3. CHLORIDE

At all locations where MTBE samples were obtained, chloride (Cl⁻) samples were collected as well. The detection limits for Cl were 1 mg/L and 0.5 mg/L for the coarse and fine grid sampling, respectively, whereas the Cl background concentration is about 2 mg/L. The Cl concentrations usually ranged from 0.6 mg/L up to 42 mg/L. One sample contained 445 mg/L Cl⁻. Since both MTBE and Cl⁻ migrate at the groundwater velocity, the MTBE/Cl⁻ ratio should remain constant if the only processes of importance are advection and dispersion. The MTBE/Cl⁻ total mass ratio at the injection time was about 0.59. Measurements during the 1988-89 sampling rounds at 6, 106, 317 and 476 days after injection yielded MTBE/Cl⁻ ratios between 0.33 and 1.0 for single samples as well as for the overall mass in the aquifer. The MTBE/Cl⁻ ratios measured during the 1995-96 sampling rounds were between 0.001 and 0.008, when only samples with more than 10 µg/L MTBE and 2 mg/L Cl⁻ (background concentration) were taken into account. These ratios are much lower than expected for conservative MTBE transport and can be interpreted as indication of relative mass loss of MTBE. However, the ratio could also be biased by mixing of additional Cl⁻ from other sources, such as the landfill leachate, into the plume. The presence of the landfill leachate plume in the study area was assessed in a subsequent study and could not be conclusively confirmed.

5.4. BTEX

For the fine grid sampling in November 1996, samples were analyzed for BTEX as well. The detection limit for benzene was 0.1 μ g/L, whereas toluene, ethylbenzene and the xylenes had detection limits of 0.01 μ g/L. Figure 5-5 shows depth integrated concentrations for total BTEX. Very low, but measurable, BTEX concentrations were found at almost all sampling locations. Except for two measurements where toluene was found at concentrations between 5 and 6 μ g/L, all other samples contained less than 5 μ g/L of the single BTEX compounds. The highest measured benzene concentration was 3.7 μ g/L, below the typical drinking water limit of 5 μ g/L.

5-6

Under aerobic conditions, BTEX usually undergoes relatively rapid biodegradation to nondetectable concentrations, i.e., it does not exhibit a minimum concentration threshold of biodegradability (e.g., Chapelle, 1992). Furthermore, BTEX is retarded within the Borden aquifer with retardation factors between 1.1 for benzene and 1.6 for p-xylene (Hubbard *et al.*, 1994). It is therefore suspected that the measured BTEX concentrations are not part of the MTBE plume introduced into the aquifer in July 1988. Thus, the origin of the BTEX measured remains unexplained.



Figure 5-5. Sampling locations with depth integrated total BTEX concentrations (mg/m²) for the fine grid sampling round.

5.5. OXYGEN

The field measurement of dissolved oxygen (DO) using the Waterloo drive-point profiling technique was more difficult than expected. It was therefore decided to install additional bundle piezometers to obtain DO profiles. Locations B, C and D in Figure 5-3 represent the positions of the bundle piezometers which provide reliable DO measurements with

5-7

a small vertical spacing of 25 cm. The bundle piezometers are permanent installations and therefore the measurements are repeatable.

For these measurements, the field CHEMETRICS[™] kit for DO was used with a detection limit of 0.1 mg/L. The measurements confirm that the aquifer contains lower oxygen concentrations close to the aquitard (Figure 5-6). This is in agreement with earlier studies which suggest a landfill leachate plume in the lower portion of the aquifer (Nicholson *et al.*, 1983). Nicholson and coworkers suggested the dilute leachate plume extends just beyond the current sampling area, about 600 meters downgradient of the landfill. However, the presence of the landfill leachate plume could not be conclusively confirmed within the present study.



Figure 5-6. Dissolved oxygen concentrations (mg/L) at various depths at locations B, C and D (see Figure 5-3) using bundle piezometers.

5.6. SULFATE

Sulfate (SO₄) is an additional indicator for the landfill leachate plume (Nicholson *et al.*, 1983), and was determined from the November 1996 sampling. The detection limit for SO₄ was 2.0 mg/L.

At most locations, the SO_4 concentration increases with depth (Figure 5-7). This could support the hypothesis that the anaerobic landfill leachate plume is present in the bottom part of the aquifer. However, a more distinct boundary between the leachate plume and the overlaying groundwater was expected. These field observations suggest that the leachate plume has become very dilute, mixed with background groundwater, and has reached a quasi-steady-state.



Figure 5-7. Examples of MTBE / Sulfate depth profiles for the transect A - A'.

5.7. AMMONIA

Salanitro *et al.* (1994, 1996) isolated a bacterial culture that biodegraded MTBE in the laboratory. They state that aerobic ammonia degraders might play an important role in the degradation process. During the November 1996 sampling round, ammonia analyses were

undertaken to investigate a possible pattern between MTBE and ammonia appearance within the aquifer. Figure 5-8 presents depth integrated ammonia concentrations based on NH₃/nitrogen in g/m^2 nitrogen (NH₃/N in g/m^2 N). The detection limit was 0.1 mg/L NH₃/N. Ammonia was found at only two locations, both outside the actual MTBE plume. Based on this limited occurrence, no interpretation can be made.



Figure 5-8. Sampling locations with depth integrated ammonia concentrations (g/m^2) for the fine grid sampling round.

Section 6 SUMMARY AND DISCUSSION

The Borden MTBE plume was characterized with three major sampling rounds (November 1995, July/August 1996 and November 1996), planned and accompanied by numerical modeling. The main goal was to delineate the MTBE plume in great enough detail to perform a reliable mass balance comparing the remaining MTBE with that originally injected in 1988. The Borden aquifer is exceptionally well characterized and the actual locations where MTBE was found are in excellent agreement with the locations suggested by numerical modeling. The MTBE concentrations measured, however, were more than an order of magnitude lower than expected based on the modeling that considered dispersion and diffusion as the only attenuation mechanisms.

All sampling found MTBE only in the deepest portion of the aquifer close to the underlying aquitard (Figure 5-4). Therefore, there is confidence that little MTBE existed above the monitoring points. Generally, non-detect levels of MTBE were found in the peripheries of the sampling grid (Figures 4-2, 5-1 and 5-2) which suggest that the lateral extent of the plume was delineated. However, although the hydraulics for this aquifer are very well known and MTBE was encountered where it was expected, there is the possibility that a portion of the plume exists outside the sampling grid.

An MTBE mass balance was attempted. Each sampling event on its own would most likely not be sufficient to perform a reliable mass balance. Based on the good match between the predicted sampling locations and the actual locations where MTBE was found, the mean groundwater velocity of about 9 cm/day holds as average velocity for the eight years of plume movement. The mean groundwater flow direction was also constant and the aquifer is fairly homogeneous. Therefore, the concentration data obtained during the November 1995 and July/August 1996 sampling rounds can be time corrected. Each depth integrated concentration value obtained during these sampling rounds is shifted based on the average groundwater velocity and flow direction to where the groundwater would have been during the final

6-1

November 1996 sampling round. Figure 6-1 shows a schematic cross section of the MTBE plume transport from injection until 1996. In Figure 6-2, the corresponding depth-integrated and time-corrected MTBE concentrations are presented in plane view for the combined 1995-96 sampling rounds.



Figure 6-1. Schematic cross section of the vertical MTBE concentration distribution from injection until 1996.



Figure 6-2. Depth-integrated and time-corrected MTBE concentrations (mg/m²) for all sampling rounds. These concentrations are used to perform the mass balance. Stars indicate sampling locations where existing multi-level piezometers were sampled in depths of 0.3 - 3.5 m below the water table.

The standard KRIGING routine together with the GRIDVOL option of GEOSOFTTM was applied to the generated concentration distribution in Figure 6-2 to calculate the total mass remaining in the plume. For the KRIGING, a spherical interpolation function was used for the variogram with a blanking distance of 50 m, a grid cell size of 2.5 m, a range of 5 m, a nugget of $0.0 (\text{mg/m}^2)^2$ and a sill of 6000 $(\text{mg/m}^2)^2$, respectively. The calculated total MTBE mass in the aquifer was only 22 g, much less than the 752 g of MTBE originally introduced in 1988. However, since a sill of 6000 $(\text{mg/m}^2)^2$ appears to be relatively high for the concentrations given, a second geostatistical method was applied to verify the calculations. The inverse distance method of the software package GMSTM was used to calculate the total mass. With this method, an MTBE mass of 24.5 g was obtained which confirms the previous results. Only about 3 percent of the initially injected MTBE mass was found.

6-3

Although the data are limited, an additional mass balance was calculated for the fine grid sampling concentration distribution alone (Figure 5-2). The inverse distance method of GMS[™] yielded a total recovered mass of about 9 g for this sampling round. This further supports the results of the total mass calculation for all three sampling rounds combined.

With full recognition of the uncertainty inherent in a field study of this nature, there is nevertheless some evidence that the Borden MTBE plume underwent significant mass loss. However, based on the apparent mass loss alone, it is not possible to conclusively prove that the major mass loss process is biodegradation. A discussion of other possible attenuation processes is provided.

Chemical degradation. To the authors' best knowledge, abiotic MTBE degradation involving subsurface material was only shown in one set of experiments by Yeh and Novak (1995). These researchers found MTBE to hydrolyze when hydrogen peroxide was added, but iron was needed to act as a catalyst. This reaction is insufficient in aerobic or near-neutral (pH > 6.5) environments (Squillace *et al.*, 1997) such as the Borden aquifer with a mean pH value of 7 - 8. The possibility of abiotic MTBE degradation at the Borden field site is therefore ruled out.

Plant uptake. At the site, two forested areas exist with predominantly Aspen and Pine trees and ferns. Contrary to a common perception, the main orientation of tree roots is horizontal, not vertical. In fact, tree roots generally spread horizontally as far as 1-3 times the tree height, while almost 90 percent of a tree's roots can be found within the upper 0.6 m of soil (Dobson and Moffat, 1995). Root growth has been found to stop completely when air space dropped to 2 percent. The reduced root growth at higher water content can be attributed to the fact that oxygen diffuses in solution about 10,000 times less rapidly than in the gas phase, thereby restricting the gas exchange in soil (Dobson and Moffat, 1995). Thus, at the Borden field site, where the top of the capillary fringe is found 2 - 3 m below ground (Figure 6-1), it is doubtful that vertical root penetration extends beyond this depth and reaches the water table. In

6-4

conclusion, it is very unlikely that plant uptake influenced the MTBE plume introduced 1.5 m below the water table.

Volatilization. MTBE has a moderate dimensionless Henry's law constant of about 0.04 (Zogorski *et al.*, 1997), expressed here as the ratio of its concentration in air to its concentration in water. As stated above, the MTBE was introduced 1.5 m below the water table and moved downwards even further during transport (Figure 6-1). No contact of dissolved MTBE with the air phase during the entire experiment occurred and, therefore, it seems very unlikely that volatilization could have been a major attenuation factor.

Sorption. Another possible attenuation factor is sorption, in form of reversible and irreversible sorption. Irreversible sorption onto soil particles was shown to be unimportant for other aquifers (e.g., Garrett *et al.*, 1986; Squillace *et al.*, 1996). In addition, Hubbard *et al.* (1994) tested Borden aquifer material in laboratory batch experiments and confirmed this observation. However, reversible sorption of MTBE could have occurred. MTBE has an organic carbon-based partition coefficient (K_{OC}) of 11 cm³/g (Zogorski *et al.*, 1997). The organic carbon content (f_{OC}) for the Borden aquifer is about 0.02 percent. Based on the following relationship:

$$K_{d} = K_{OC} \cdot f_{OC} \tag{6-1}$$

a distribution coefficient K_d can be calculated as about 0.0022 cm³/g. Hence, with

$$\mathbf{R} = 1 + \left(\rho_{\rm b} \ \mathbf{K}_{\rm d}\right) / \theta \tag{6-2}$$

a retardation factor can be obtained (Higgins, 1959), where ρ_b is the bulk density of the aquifer material and θ is the porosity. For the Borden aquifer, ρ_b is about 2.67 g/cm³ and θ is 0.33. The resulting retardation factor is 1.02, which implies that only about 15 g or 2 percent of the initial 752 g of MTBE are sorbed onto aquifer material. This low value cannot account for the huge discrepancy of initial and final MTBE mass observed in the study site aquifer.

The interpretation of major MTBE mass loss by 1995-96 (7-8 years after injection) seems to contradict the suggestion of its conservative behavior during the initial 476 days of transport (Hubbard *et al.*, 1994). The trend in the recovered mass in the aquifer over the initial 476 days of the experiment will be reviewed. Figure 2-5 shows the Cl⁻ corrected MTBE mass for all initial sampling rounds. Using the statistical program SYSTAT[™], a regression line for the data was calculated resulting in the following equation:

Mass of MTBE (time) =
$$736 \text{ g} - 0.327 \text{ g/day} \cdot \text{time}$$
 (in days) (6-3)

The slope of 0.327 g/day was found to be significant at a level of alpha = 0.1 (Figure 6-3). This interpretation suggests that there was a small but statistically significant mass loss during the first 476 days of the MTBE monitoring.

Figure 6-3 shows the recovered mass of the initial sampling rounds as well as the mass of the final round. The regression line is shown for the initial mass estimates. The slope of the line through the initial and final mass is 0.243 g/day and therefore slightly flatter than the slope of the regression line with 0.327 g/day. These should be interpreted as apparent mass loss rates and should not be taken as the actual rate of biodegradation.

In Figure 6-3, the MTBE mass estimates for the initial sampling rounds were corrected as discussed in Section 2. This procedure excludes pure dilution (diffusion/dispersion) as a significant attenuation process for MTBE. This, in turn, could suggest that biodegradation might have played an important role in the MTBE attenuation since the MTBE mass appears to decrease over time. However, if MTBE degradation were occurring, it was much slower than that of the BTEX compounds (Figure 2-4). Other possible reasons for a slow MTBE degradation rate will be discussed.



Figure 6-3. MTBE field mass estimates with the initial sampling rounds (up to 476 days) and the final sampling round about eight years (3000 days) after injection. The dashed line represents the regression line based on the initial sampling rounds up to 476 days only.

Oxygen limitations in the beginning of the Borden field experiment due to the preferred aerobic degradation of the BTEX could have slowed the initial MTBE degradation. Furthermore, this apparent time lag (adaptation time) in the degradation could have been caused by a very small initial microbial degrader population requiring considerable time to produce sufficient biomass to generate significant MTBE mass removal. Salanitro *et al.* (1994, 1996) report adaptation times of up to six months in their microcosms before degradation occurred. Since plumes in the field are long (Figure 2-1) and the groundwater flow velocity is low (only about 9 cm/day or 33 m/year), the microbial population within a certain part of the aquifer has a long time to adapt to a new substrate such as MTBE. Another cause of an overall slow degradation rate could be that MTBE is toxic to the microorganisms at high concentrations (Salanitro, 1996). This could mean that MTBE is only degraded at the edges of the plume where concentrations are relatively low (< 1 mg/L) or after considerable transport and dispersion have lowered MTBE concentrations.

6-7

Another possible cause of the apparent MTBE recalcitrance over the initial 476 days of plume movement could be substrate competition. Perhaps BTEX had to be removed first before MTBE would be used as substrate by the microorganisms.

MTBE was only found close to the bottom of the aquifer where the anaerobic landfill leachate plume was expected. Perhaps MTBE biotransformation was slowest in this anaerobic zone. The oxygen profiles show lower oxygen concentrations within this part of the aquifer (Figure 5-6). Possible additional indicators for the presence of the landfill leachate plume are increased chloride and sulfate concentrations. However, the chloride concentrations (not shown) have no obvious vertical trend. Sulfate concentrations, on the other hand, are higher in the bottom part of the aquifer (Figure 5-7) but the data do not conclusively confirm that the leachate plume is present.

No sample contained TBA or TBF, two potential MTBE degradation products. Perhaps these products are formed during MTBE biodegradation, but are transformed or mineralized quickly. But no firm support can be drawn for MTBE biodegradation.

No ammonia was found at any locations where MTBE was encountered. Ammonium utilizing microorganisms could play a role in MTBE degradation (Salanitro *et al.*, 1996). Therefore, this observation might suggest that wherever ammonia was available, it has been used to generate biomass. However, it might also mean that ammonia was never present in that part of the aquifer.

In summary, the presented results provide some evidence for natural attenuation including a mass removal component. While a number of processes that could have produced this apparent mass loss (irreversible sorption, volatilization, plant uptake) are discounted, it is always possible that a large portion of the MTBE mass was not sampled in 1995-96. However, it is also possible that biodegradation accounted for the removal of 97 percent of the MTBE within the Borden aquifer over the 8 year experiment. However, only weak support for biodegradation could be developed. Therefore, additional research is needed to confirm the role of biodegradation in the

6-8

attenuation of MTBE in the Borden aquifer. Studies are underway, but no confirming laboratory evidence has been found to date (Hubbard *et al.*, 1994; Salanitro, 1997; Javanmardian, 1997). Therefore, biodegradation as the process cannot yet be confirmed.

Section 7 FUTURE WORK

The work described in this report focused on a field experiment. No firm conclusion in terms of MTBE field biodegradation can be drawn from this evaluation alone. Additional work at this site will focus on further investigation of the Borden field experiment: (1) some additional field monitoring, and (2) laboratory microcosm experiments using Borden aquifer material and groundwater samples.

At locations B, C, and D (Figure 5-3) multi-level bundle piezometers with a vertical spacing of 25 cm have been installed. The bundles B and C are where MTBE has been found using the Waterloo drive-point profiling technique. With these bundles, confirmation could be obtained that the vertical spacing of 0.5 - 1.5 m for the major sampling rounds was sufficient in characterizing the plume vertically and that no high concentrations were missed in between the sampling points. Furthermore, confirmation could be obtained that no slow moving MTBE slug is present within the aquifer. Since the bundle at location D has been installed between two recent MTBE discoveries, this bundle could confirm that the chosen transverse grid spacing was sufficient to delineate the plume.

In addition, soil cores and groundwater samples have been taken at location B. The core material and the water samples have been sent to three laboratories [Oregon Graduate Institute, University of Bradford (UK), and the Department of Biology at the University of Waterloo]. Laboratory microcosm and column experiments are underway to investigate the biodegradation ability of the Borden microbial consortium.

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R-2

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R-3

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Appendix A

PRELIMINARY MODELING AND RESULTS OF THE 1995 SAMPLING ROUND

RATIONALE AND OBJECTIVES

About 2,800 L of groundwater containing about 515 mg/L Cl⁻, about 18 mg/L BTEX and 270 mg/L MTBE were injected into the Borden aquifer on July 13, 1988 (Hubbard *et al.*, 1994). MTBE was found to be conservative (i.e., it migrates as fast as groundwater and showed no evidence of significant mass loss). Groundwater monitoring ended in November 1989, 476 days after injection. The objective of the 1995/96 sampling round was to determine if the remaining MTBE plume can be found within the Borden aquifer.

The plume had migrated into an unmonitored section of the Borden aquifer. Further, both solutes, MTBE and Cl⁻, have undergone dispersive dilution. These factors made it problematic to find the plume and made it extremely difficult to quantify the mass of MTBE remaining. However, if both MTBE and Cl⁻ can be found above background concentrations, then the ratio of MTBE to Cl⁻ may reflect any mass loss that MTBE has undergone. Since both MTBE and Cl⁻ migrate at the groundwater velocity, the MTBE/Cl⁻ ratio should stay constant if the only processes of importance are advection and dispersion. On the other hand, if MTBE is being transformed or degraded, this ratio should decrease. This appendix evaluates the MTBE/Cl⁻ ratio to study the long term fate of MTBE.

MODELING OF THE MTBE/CL' PLUME BEHAVIOR

The analytical model SLUG3D (Sudicky, 1985) was used to simulate transport of MTBE and Cl⁻ over the 2700-day period from the injection up to November 1995. The transport parameters used correspond with previously calibrated values (Schirmer *et al.*, 1995) and are as follows:

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| Velocity | v | = | 0.095 m/day |
|------------------------------------|---------------|---|--|
| Porosity | θ | = | 0.33 |
| Longitudinal Dispersivity | α_{L} | = | 0.25 m |
| Horizontal Transverse Dispersivity | α_{TH} | = | 0.02 m |
| Vertical Transverse Dispersivity | α_{TV} | = | 0.005 m |
| Effective Diffusion Coefficient | D* | = | 7.5 x 10 ⁻⁵ m ² /day |

The regional flow at the site is predominantly to the north (Frind and Hokkanen, 1987). The flow field shifts over the seasons. However, all previous workers (e.g., Mackay *et al.*, 1986; Patrick *et al.*, 1986; Hubbard *et al.*, 1994) noted a consistent mean flow direction to the north at least over the initial 100 m of tracer movement. This uncertainty was accounted for by considering a variation of 5° to the west and to the east with respect to the generally north flow direction (Figure A-1). The plumes of Figure A-1 represent the 1 mg/L MTBE contour lines of the expected plume locations by using an average velocity of 8.5 cm/day, 9.5 cm/day, and 10.5 cm/day, respectively. The center of mass moved 227.5 m, 252.5 m and 280.0 m, respectively, depending on the velocity assumed. The 1 mg/L contour line extends approximately 33 m in flow direction and 10 m in the horizontal transverse direction. The vertical extent of the plume near the center of mass can be expected to be a little less than 5 m. The calculated peak concentrations are approximately 3 mg/L for MTBE and 5 mg/L for MTBE and Cl⁻, respectively. (The calculation procedure of depth integrated concentrations is discussed in Section 2.)

A-2



Figure A-1. The three plumes represent the 1,000 μ g/L MTBE contour lines for flow velocities of 8.5 cm/day, 9.5 cm/day, and 10.5 cm/day, respectively, at 2680 days after injection. The straight dashed lines illustrate a uncertainty of \pm 5° in the flow direction.

A comparison of the simulation results to the field data of 476 days was conducted. The measured data show slightly higher concentrations than those obtained by SLUG3D. This discrepancy could mean that the calibrated dispersivities are too high and therefore the real plume at 2700 days is more compact than that shown in Figure A-1. A more compact plume would yield higher peak concentrations than the projected 3 mg/L MTBE and 5 mg/L Cl⁻.

The plume has migrated close to an area used periodically for pumping test research and demonstration (see Pumping Test Site - Figure A-1). There is the possibility that pumping may have altered the actual position of the plume. Because Conant's pumping tests (Figure A-1) ended in 1991, there is very little chance that these tests could have affected the plume migration since the MTBE/Cl⁻ plume would not have been within the area of influence in 1991. However, one pumping test over two days is conducted every year for teaching purposes at the test site.

A-3

The pumping rate is approximately 60 L/min. An evaluation of particle travel times, using the 2D numerical model FLOWPATH (Franz and Guiguer, 1995), was conducted. It was calculated that it is extremely unlikely that these pumping tests have had a large influence on the movement of the MTBE/Cl⁻ plume. However, pumping may have induced some mixing of the MTBE/Cl⁻ plume with the underlying landfill leachate plume which contains Cl⁻, but no MTBE. This could reduce the probability of finding the MTBE plume and may complicate the interpretation of MTBE/Cl⁻ ratios.

ANTICIPATED EFFECTS OF PUMPING TESTS ON THE MTBE PLUME MOVEMENT

The two-dimensional numerical model FLOWPATH (Franz and Guiguer, 1995) was used to investigate the possible influence of pumping tests on the movement of the MTBE plume. Aquifer parameters were evaluated using pumping test and slug test data gathered in a field investigation conducted April 22-29, 1994. Slug test results obtained from monitoring wells distributed over the study area gave reasonable hydraulic conductivity values in comparison to the pumping test conducted at that time. A review of historical data and the aquifer tests mentioned earlier indicate that the hydraulic conductivity is in the order of 1 to 10 m/day over the entire site.

The hydraulic gradient used in the FLOWPATH simulations was evaluated from static water level measurements during the field investigation. The gradient was projected across the site to generate a static water table map. The hydraulic gradient calculated was 0.0044. FLOWPATH was used to simulate steady-state conditions with the actual pumping test rate of 57 L/min. The model was calibrated using final drawdown values in seven observation wells. It was assumed that near steady state conditions had been reached at these monitoring points.

Aquifer tests indicated an initial hydraulic conductivity of 8 m/day. A recharge value of 0.15 m/year was used (Regional Municipality of Waterloo, 1991). The model was calibrated through adjustments in hydraulic conductivity since it was assumed that hydraulic conductivity

STD.API/PETRO PUBL 4668-ENGL 1998 🗰 0732290 0611424 375 🗰

was the most uncertain parameter. The final calibrated aquifer parameters for hydraulic conductivity and recharge are 3.51 m/day and 0.15 m/year, respectively.

A capture zone/pathline analysis has been conducted using the calibrated model in order to estimate the anticipated influence of the pumping test. Even if these two-day pumping tests each year had run for one full year, no measurable influence on the MTBE plume movement would have occurred. These modeling results are in agreement with the results of the two-day pumping test April 23-25, 1995. The radial drawdown cone extends less than 8 m after two days of pumping. Therefore, it is assumed that the short term pumping tests had no significant influence on the movement of the plume.

The Conant pumping test in 1991 lasted less than two weeks. Considering all uncertainties with respect to flow direction and velocity, there is very little chance that this pumping test could have affected the movement of the MTBE plume significantly.

SAMPLING GRID DESIGN

It was planned to sample at 24 locations. Due to greater uncertainty with respect to the flow direction compared to the flow velocity, transverse sampling across the projected plume width was emphasized. Locations are shown in Figure A-2. In order to capture the plume, the distance between the wells is commonly 8 m.



Figure A-2. The three plumes represent the 1,000 µg/L MTBE contour lines for flow velocities of 8.5 cm/day, 9.5 cm/day, and 10.5 cm/day, respectively, at 7 years and 4 months after injection. The straight dashed lines illustrate a uncertainty of 10° in the flow direction. The dots represent the proposed sampling locations.

Since the solute was injected 1.5 m below the water table and moved slightly downwards (Hubbard *et al.*, 1994) due to recharge, 4 samples vertically per location were proposed with 1.5 m spacing starting at 1.5 m below the water table. It has to be kept in mind that the study area is partly covered by pine forests. Therefore, the sampling points were subject to change due to accessibility problems. The actual sampled locations were reported for further reference and the following calculations.

RESULTS OF THE 1995 SAMPLING

Plume sampling was conducted during two sampling rounds on November 18-19 and November 26-27, 1995. Sampling was carried out at three depths at 13 locations rather than at 24 locations as proposed. Reduction of the number of sampling points was due to hard layers and boulders in the investigation area. Freezing weather made sampling difficult.

Sampling locations and MTBE concentrations are shown in Figure A-3. Thirty-six samples, 6 duplicates, 4 field blanks, and 1 trip blank were collected for MTBE. Cl⁻ samples were collected at 35 levels. One level could not be sampled.

Analytical results show that part of the original MTBE plume was found (Figure A-3). Sampling locations, particularly towards the center of the transect, contained MTBE as predicted by the mathematical simulations. The plume also appeared to be slightly towards the east of the projected location. The highest MTBE concentration found was 190 μ g/L. No conclusion could be drawn regarding whether the center or the periphery of the plume had been located.

All samples were also analyzed for BTEX compounds. One sample contained 1.3 μ g/L xylenes. Six samples contained toluene above the detection limit of 1 μ g/L, with the highest concentration being 1.8 μ g/L. No benzene and ethylbenzene were detected.

The MTBE/Cl⁻ total mass ratio at the injection time (July 1988) was approximately 0.56. Total solute mass calculations at sampling rounds 6, 106, 317, and 476 days after injection yielded MTBE/Cl⁻ ratios between 0.33 and 1.0 for single samples as well as for the overall mass in the system. The November 1995 results, however, show MTBE/Cl⁻ concentration ratios from 0.005 to 0.008 (only samples with more than 10 μ g/L MTBE and 2 mg/L Cl⁻, background concentration, have been considered). This suggests that MTBE may have undergone transformation, traveled at a slower velocity than the Cl⁻, or additional Cl⁻ from other sources was introduced into the aquifer. A combination of the above may have occurred.

STD.API/PETRO PUBL 4668-ENGL 1998 📰 0732290 0611427 084 📰



Figure A-3. MTBE sampling results with obtained peak concentrations from the November 1995 sampling round. The three plumes represent the 1000 µg/L contour lines for average groundwater velocities of 8.5 cm/day, 9.5 cm/day, and 10.5 cm/day, respectively.

A-8

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Appendix B

TWO-DIMENSIONAL MODELING USING RANDOM HYDRAULIC CONDUCTIVITY FIELDS

REVIEW AND SUMMARY OF 1995 SAMPLING RESULTS

It is difficult to draw conclusions from the 1995 results since it is doubtful that the plume has been accurately delineated. The expected peak concentrations of MTBE, based on the analytical solution SLUG3D (Sudicky, 1985), were more than 3 mg/L. Measured MTBE concentrations were less than 200 μ g/L. The expected Cl⁻ peak concentrations, using the analytical solution with the same hydraulic parameters as for MTBE and the Cl⁻ input concentration of 515 mg/L, were about 5 mg/L (Cl⁻ background concentration is about 2 mg/L). The main portion of the analyzed Cl⁻ samples shows higher concentrations than the simulated 5 mg/L. While these limited data provide a speculative suggestion that MTBE could have been biodegraded and/or retarded, no firm interpretation of the fate of the original MTBE plume is possible.

Therefore, it was proposed to initiate a second, more comprehensive sampling round in order to quantify the remaining MTBE mass within the aquifer. Numerical 2D modeling to determine the anticipated uncertainty with respect to the actual plume location was suggested. The simulation results are summarized in the following section.

2D MODELING OF THE MTBE DISTRIBUTION 8 YEARS AFTER INJECTION

In order to achieve more realistic results, three 2D random hydraulic conductivity fields were generated using identical statistical parameters for the Borden aquifer. The numerical code FGEN92 (Robin *et al.*, 1993) was applied to create the random hydraulic conductivity fields. The aquifer parameters used are given by Woodbury and Sudicky (1991) and are as follows:

| Horizontal Correlation Length (in x- and y-Direction) | $\lambda_{\rm X} = \lambda_{\rm Y} = 5.14 \ {\rm m}$ | | |
|---|--|---|--|
| Variance | Y^2 | = 0.244 | |
| Mean Hydraulic Conductivity | K | $= 9.32 \text{ x } 10^{-5} \text{ m/s}$ | |

The numerical program WATFLOW-3D (Molson *et al.*, 1995) was used to generate the flow field based on the random hydraulic conductivity distribution and the following aquifer parameters:

| Porosity | θ | = 0.33 |
|--------------------|--------|-----------|
| Hydraulic Gradient | grad h | = 0.00369 |

The resulting mean velocity is approximately 0.09 m/day.

The numerical model BIO3D (Schirmer *et al.*, 1995) was then applied to simulate transport of MTBE over the 2920-day period from the injection up to 1996. The transport parameters correspond with previously calibrated values (Schirmer *et al.*, 1995) and are as follows:

| Longitudinal Dispersivity | α_L | = 0.25 m |
|------------------------------------|-----------------------|---|
| Horizontal Transverse Dispersivity | α_{TH} | = 0.02 m |
| Effective Diffusion Coefficient | D* | $= 7.5 \text{ x } 10^{-5} \text{ m}^2/\text{day}$ |
| Initial MTBE Source Concentration | c ₀ | = 290 mg/L |

As previously stated, MTBE was assumed to be conservative and to have a retardation factor of 1. It should be noted that 45,000 elements were required to simulate the given problem in 2D. Far more than one million elements would be needed to perform 3D simulations and this is beyond the authors' current computational capabilities.

RESULTS OF THE 2D MODELING

The anticipated plume location for 2920 days (8 years) after injection was simulated (Figure B-1). Although the identical statistical and hydraulic parameters were used for the

B-2
simulations, the center of mass for the plumes are found at quite different locations. The center of mass for realization 3 traveled only about 250 m, whereas realization 2 shows the center of mass at approximately 276 m. The calculated MTBE peak depth integrated concentration of more than 4 g/m² corresponds well with previous simulations using the analytical solution SLUG3D (Sudicky, 1985). Given this uncertainty of the plume location, locating and characterizing the MTBE plume required a broad distribution of sampling locations.



Figure B-1. Anticipated plume locations for three realizations using identical statistical aquifer parameters with the MTBE sampling results from the November 1995 sampling round (as depth integrated concentrations in mg/m²). The three plumes represent the 500 mg/m² contour lines for an average groundwater velocity of approximately 9 cm/day.

STD.API/PETRO PUBL 4668-ENGL 1998 📰 0732290 0611432 441 📖

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Appendix C

DETERMINATION OF THE OPTIMAL GRID SPACING USING GEOSTATISTICAL METHODS

INTRODUCTION

The task of this part of the project was to locate the anticipated plume based on the modeling results and previous work at the Borden field site. An approximate sampling grid including the required sampling depths for the field data collection was also determined. Since it is currently impossible to perform a 3D simulation for 2920 days (8 years), it was decided to carry out a 2D calculation, again using a selected random hydraulic conductivity field (Woodbury and Sudicky, 1991). This simulation is based on depth integrated MTBE concentrations in the 2D domain which can be used to find an optimal sampling grid design. Since the previous plumes generated using random hydraulic conductivity fields (RHC fields) (Appendix A) yielded lower peak concentrations than those observed at 476 days (last sampling round of Hubbard et al., 1994), more RHC fields were generated and the resulting plumes at 476 days were compared to the field measurements. The simulation which best reproduced the field results was then run to 2920 days simulation time to provide a realistic distribution of the expected MTBE plume in the summer 1996 (Figure C-1). The KRIGING routine together with the GRIDVOL (grid volume) option of the geostatistical software package GEOSOFT[™] was then applied to this plume to determine the "recovered" total mass in the domain for each individual sampling grid. For the KRIGING, a spherical interpolation function was used with a blanking distance of 50 m, a grid cell size of 2.5 m, a range of 5 m, a nugget of 0.0 $(mg/m^2)^2$ and a sill of 2.0 $(mg/m^2)^2$.

SAMPLING DEPTHS AND GRID DESIGN

Sampling Depths

It is now generally accepted that the transverse vertical dispersion of contaminants in natural aquifers is minimal (e.g., Woodbury and Sudicky, 1991). This observation was confirmed

STD.API/PETRO PUBL 4668-ENGL 1998 📰 0732290 0611434 214 📰

during the first 476 days of plume development (Hubbard *et al.*, 1994). It is believed that the additional vertical spreading of the MTBE plume during the subsequent 8 years of movement through the aquifer will be minor. Therefore, 3-4 sampling depths were proposed per sampling location as sufficient to delineate the vertical extent of the plume during the initial coarse grid sampling. It should be noted that the KRIGING routine of GEOSOFT[™] does not require the exact edge of the plume (concentrations of zero) in order to calculate reliable estimates of the mass in the system. However, a larger number of sampling depths might be required during the secondary fine grid sampling round. This was determined after the coarse grid sampling was evaluated.

A preliminary sampling using bundle piezometers in May 1996 found measurable MTBE concentrations only 3.5 meters below the water table and deeper. The last sampling round, 476 days after injection, shows a vertical plume extent of about 3.0 to 3.5 meters, starting 2 meters below the water table (Hubbard *et al.*, 1994). Therefore, sampling depths of 3.5, 5.0, 6.5, and possibly 8.0 meters below the water table were proposed for the coarse grid sampling.

Sampling Grid Design

The total mass of MTBE in the domain was known from the numerically generated plume (Figure C-1). It was then possible to test different sampling grid designs to determine the recovery of total mass in the system. Three different spacings in longitudinal (20 m, 15 m, and 10 m) and transverse direction (10 m, 7.5 m, and 5 m), respectively, were applied. As expected, the fewer sampling points located within the plume, the less mass recovered. This was tested by removing transects of sampling points around the edge of the plume for each individual sampling grid. Since the generated plume is long and thin, the mass recovery was much more sensitive to the transverse spacing than to the longitudinal one.

C-2



Figure C-1. Anticipated plume location with known MTBE mass using a 2D numerical simulation with a random hydraulic conductivity field which reproduced the field measurements at 476 days very well. The plume contour lines are 3000, 1000, and 500 mg/m². The obtained concentrations are depth integrated in mg/m².

A longitudinal spacing of 20 m in the flow direction using transverse spacings of 7.5 and 10 m, respectively, were evaluated. Up to 30 sampling locations were regularly placed over an area sufficient to cover the plume. The mass recovery was larger than 95 percent if at least one sampling location was within or in close vicinity of the center of the plume (Table C-1). For the case of 5 m spacing in transverse direction, a mass recovery of more than 70 percent was obtained for any grid (Table C-1), regardless of whether the plume center was directly encountered or not.

C-3

Table C-1. Recovered MTBE mass using the KRIGING routine of GEOSOFT[™] for a longitudinal grid spacing of 20 meters. Up to 30 sampling locations were placed over an area sufficient to cover the plume.

| Transverse Spacing | Lowest Mass Recovered | Highest Mass Recovered |
|--------------------|-----------------------|------------------------|
| 10 m | 36% | 95% |
| 7.5 m | 40% | 97% |
| 5 m | 71% | 98% |

A longitudinal 15 m grid spacing in flow direction with transverse spacings of 7.5 and 10 m improved the mass recovery slightly (Table C-2) in comparison to the 20 m longitudinal spacing. In this case, up to 42 sampling locations were placed over an area sufficient to cover the plume. However, even here a significant proportion of the mass can be missed (Table C-2). A 5 m spacing in the transverse direction assures a mass recovery of more than 75 percent (Table C-2). Note that a mass recovery of more than 100 percent indicates an overestimation of the mass present in the plume using the interpolation routine.

Table C-2. Recovered MTBE mass using the KRIGING routine of GEOSOFT[™] for a longitudinal grid spacing of 15 meters. Up to 42 sampling locations were placed over an area sufficient to cover the plume.

| Transverse Spacing | Lowest Mass Recovered | Highest Mass Recovered |
|--------------------|-----------------------|------------------------|
| 10 m | 39% | 99% |
| 7.5 m | 52% | 99% |
| 5 m | 77% | 102% |

Potentially missing a significant portion of the mass for transverse spacings of 7.5 and 10 m, respectively, cannot be overcome using a **longitudinal grid spacing of 10 m** (Table C-3). A satisfactory mass recovery of more than 90 percent was obtained only by applying a 5 m spacing in the transverse direction (Table C-3). Nevertheless, the mass recovery for a longitudinal spacing of 10 and 15 m, respectively, was not greatly improved in comparison to the 20 m spacing. It has to be pointed out that up to 55 sampling locations are needed for this spacing, but only up to 30 locations are needed for a longitudinal spacing of 20 m to sufficiently cover the plume.

Table C-3. Recovered MTBE mass using the KRIGING routine of GEOSOFT[™] for a longitudinal grid spacing of 10 meters. Up to 55 sampling locations were placed over an area sufficient to cover the plume.

| Transverse Spacing | Lowest Mass Recovered | Highest Mass Recovered |
|--------------------|-----------------------|------------------------|
| 10 m | 44% | 102% |
| 7.5 m | 49% | 103% |
| 5 m | 91% | 100% |

The anticipated plume location based on the simulated realization is shown in Figure C-1. According to the results above, it was suggested to sample a coarse grid of 100 m x 40 m using a spacing of 20 m in the longitudinal and 10 m in the transverse direction, respectively (Figure C-2). This results in 30 sampling locations (50 percent of the proposed 60 sampling locations in total) and was expected to adequately locate the plume. The grid was shifted slightly closer to the original source; the reason being that several recent studies at the Borden site suggested somewhat lower average groundwater velocities than 9 cm/day (e.g., Rivett *et al.*). The finer grid employed for the second sampling round was refined based on the field results from the coarse grid sampling.

C-5



Figure C-2. Sampling locations for the coarse grid sampling round. A longitudinal spacing of 20 meters and a transverse spacing of 10 meters were chosen. The plume contour lines are 3000, 1000, and 500 mg/m² as depth integrated concentrations. The obtained concentrations from the November 1995 sampling round are also given in mg/m².

C-6

STD.API/PETRO PUBL 4668-ENGL 1998 🚥 0732290 0611439 876 🖿

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C-7

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