

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

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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-butyl-ether (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 Cl^- 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/ Cl^- 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 GEOSOFTM and GMSTM. 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.

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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 µg/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 µg/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/ Cl^- was about 0.59 initially and remained about the same until day 476 when it had decreased to 0.43. The MTBE/ Cl^- 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

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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$), 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 $\mu\text{g/L}$; field sampling found maximum concentrations of less than 200 $\mu\text{g/L}$. 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.

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 ($\text{pH} > 6.5$) 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

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.

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 $\mu\text{g/L}$; field sampling found maximum concentrations of less than 200 $\mu\text{g/L}$. 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.

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, $(\text{CH}_3)_3\text{C}(\text{OCH}_3)$] 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 $\mu\text{g/L}$. 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 cm^3/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

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 ($> 10 - 20 \text{ mg/L}$), 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 $< 15 \text{ } \mu\text{g/L}$, 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

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 µg/L have been found, when concentrations far above 1000 µg/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.

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:

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

- where C_{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}),
 c_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/m^3 times meters) which is equal to g/m^2 , or $\mu\text{g/L}$ times meters (mg/m^3 times meters) which is equal to mg/m^2 , respectively.

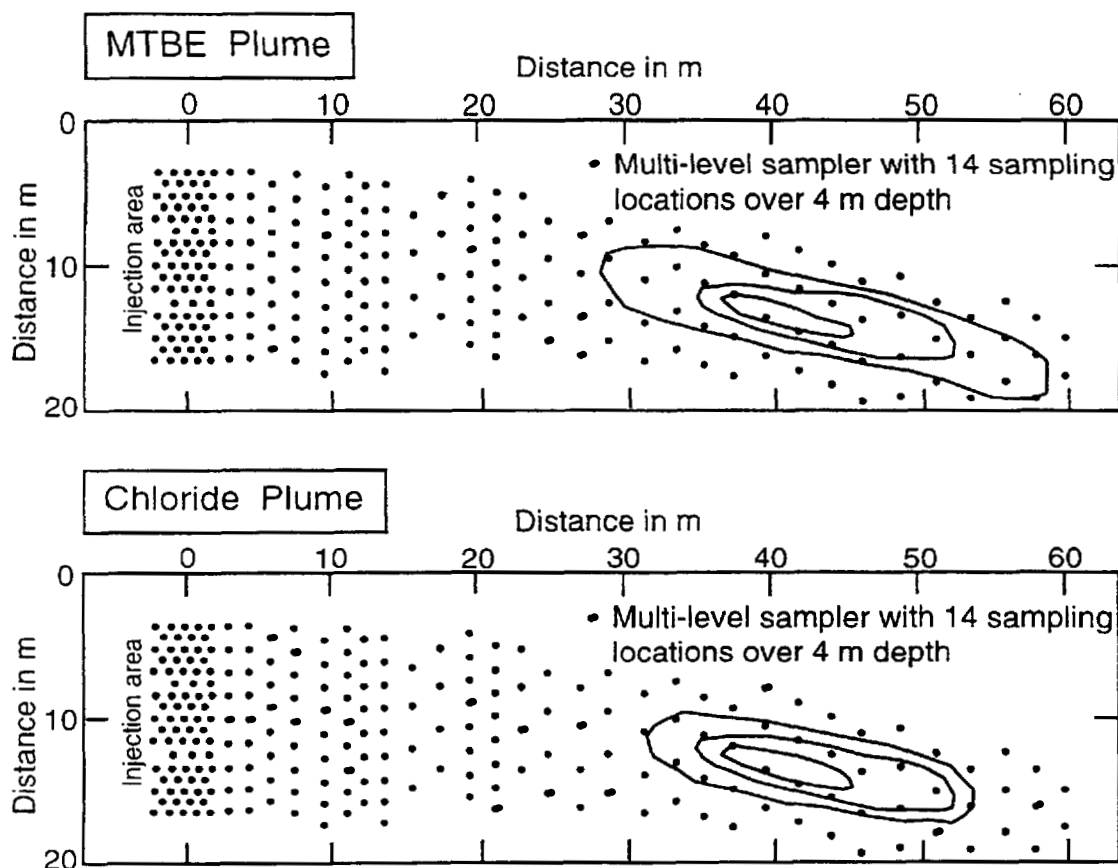


Figure 2-1. Plan view position of the MTBE plume (upper) and the Cl^- plume (lower) 476 days after injection. Contours are vertically integrated concentrations. For Cl^- , contours are 10, 20, and 50 g/m^2 , while MTBE contours are 1, 20, and 50 g/m^2 .

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/Cl⁻, 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 Cl⁻, 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:

$$\text{Total mass} = \text{Mass in solution} \times \text{Retardation factor} \quad (2-2)$$

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).

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

	Initial Conc. (mg/L)	Mass (g)						
		Day 0	Day 6	Day 42	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

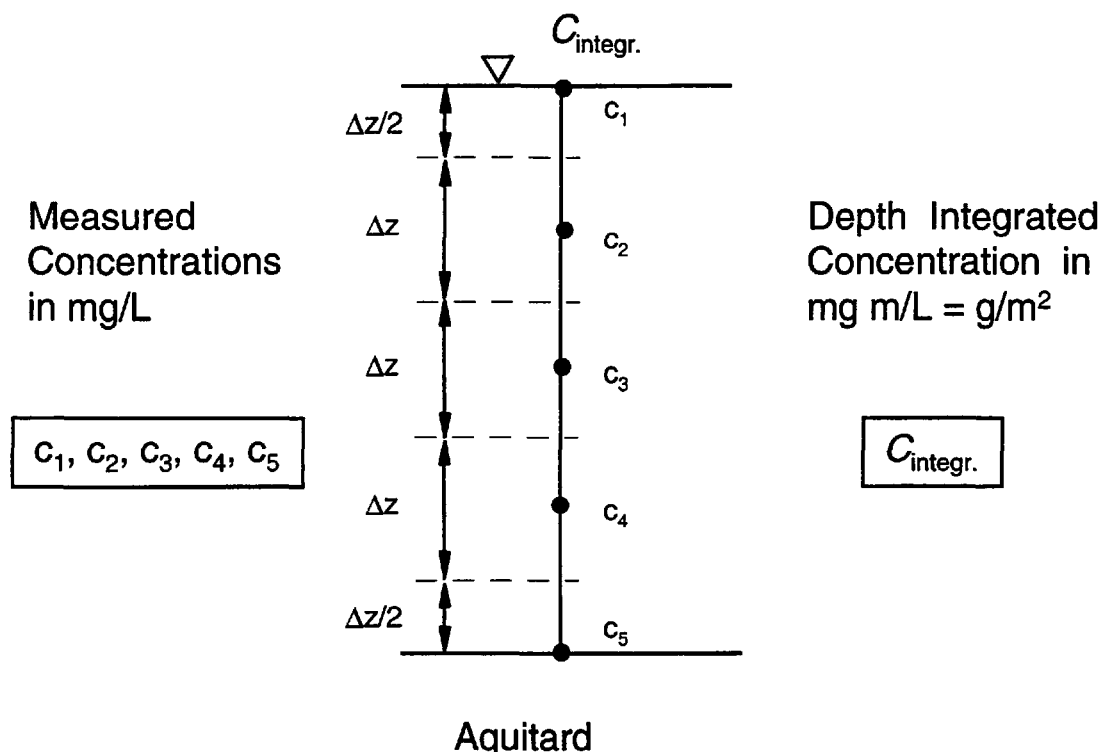


Figure 2-2. Calculation of depth integrated concentrations using vertically distributed concentrations at a single sampling location. An example calculation using Equation 2-1 with $c_1 = 5 \text{ mg/L}$, $c_2 = 10 \text{ mg/L}$, $c_3 = 12 \text{ mg/L}$, $c_4 = 14 \text{ mg/L}$, $c_5 = 3 \text{ mg/L}$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

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

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.

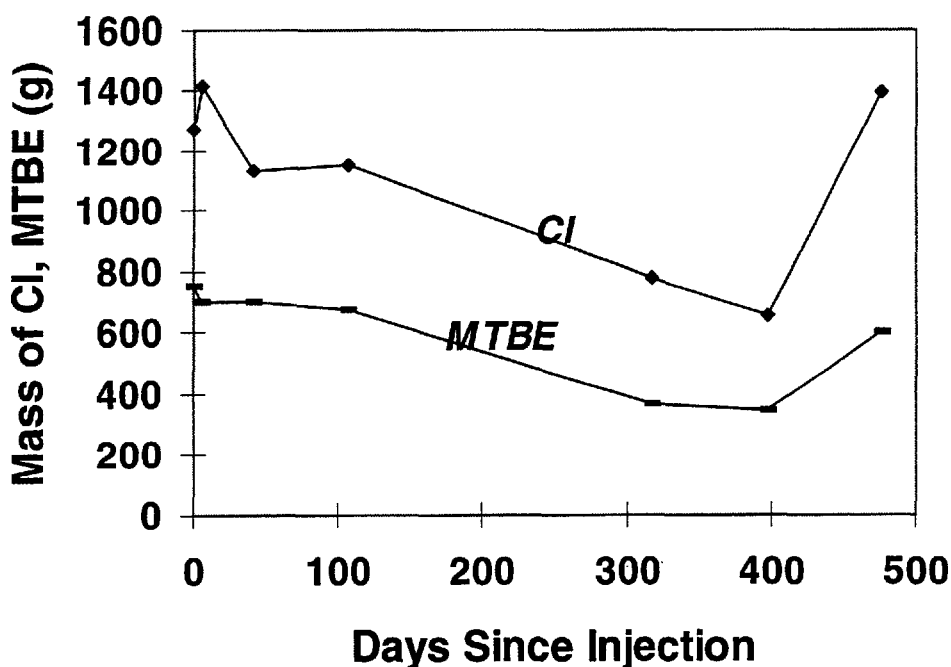


Figure 2-3. Mass of MTBE and Cl^- in the MTBE slug over the initial 476 days of snapshot monitoring.