

Natural attenuation of MTBE at two petroleum-hydrocarbon spill sites

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Abstract

Methyl tert-butyl ether (MTBE) has been used as a gasoline additive to improve the combustion efficiency and to replace lead since 1978. Because it is widely used and it has been disposed inappropriately, MTBE has become a prevalent groundwater contaminant worldwide. In this study, two petroleum-hydrocarbon contaminated sites (Sites A and B) were selected to evaluate the occurrence and effectiveness of natural attenuation of MTBE at these two sites. Field investigation results indicate that the natural attenuation mechanisms of MTBE at both sites were occurring with the first-order attenuation rates of 0.0021 and 0.0048 day^{-1} at Sites A and B, respectively. Results also reveal that the intrinsic biodegradation pattern was the most important mechanism among the natural attenuation processes at both sites. Results from BIOSCREEN simulation suggest that biodegradation was responsible for 78 and 59% of MTBE mass reduction at Sites A and B, respectively. Investigation results show that MTBE plume at Site B could be effectively controlled via natural attenuation processes. However, MTBE plume at Site A has migrated to a farther downgradient area and passed the boundary line of the site. Thus, more active groundwater remedial technologies should be applied at Site A to protect the downgradient environment. Results from this study suggest that natural attenuation might be feasible to be used as a remedial option for the remediation of MTBE-contaminated site on the premise that (1) detailed site characterization has been conducted and (2) the occurrence and effectiveness of natural attenuation processes have been confirmed.

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1. Introduction

Methyl tert-butyl ether (MTBE) has been used as a gasoline additive since 1978 to enhance the combustion efficiency and improve air quality. Since 1990, the use of MTBE has increased dramatically because of the initiation of the Oxyfuel Program in 1992 and the Reformulated Gasoline (RFG) Program in 1995. The Oxyfuel Program demanded that 2.7% of oxygen by weight should exist in gasoline during the winter months to reduce the emissions of carbon monoxide in the specific metropolitan areas and the RFG Program required that 2% of oxygen by weight should exist in gasoline throughout the year in the areas with serious ozone and smog problems [1]. Although many oxygenates such as ethanol (EtOH), ethyl tert-butyl ether (ETBE), methanol, diisopropyl

ether (DIPE), tert-butyl alcohol (TBA), and tert-amyl methyl ether (TAME), can serve as the gasoline additive, MTBE is the most commonly used oxygenate due to its easy production, convenience transportation, and acceptable price [1–3].

MTBE has become a common groundwater contaminant as a result of its wide usage and inappropriate disposal. It has been temporarily classified to the possible human carcinogen by the US Environmental Protection Agency (US EPA). An advisory level for drinking water at 20–40 $\mu\text{g/L}$ is set to protect human from adverse health effects [1]. In Taiwan, Taiwan Environmental Protection Administration (TEPA) has also classified MTBE as the Class IV toxic chemical substances. The Class IV toxic chemical substances are defined as those chemical substances that may pollute the environment or endanger human health [4,5]. Although the ban of MTBE use is under evaluation by the TEPA, no criterion for MTBE is established up to now. Thus, MTBE is not a regulated compound in the “Soil and Groundwater Remediation

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Act' which was established in the year of 2000 by TEPA. The particular characters of MTBE make its behavior in the subsurface different from other gasoline components benzene, toluene, ethylbenzene, and xylenes (BTEX). MTBE is a highly water soluble and low adsorption compound in comparison with BTEX. The biodegradability of MTBE is low due to the stable ether linkage and tert-butyl structure. Thus, it usually migrates a longer distance than BTEX and results in more difficult for remediation of gasoline-contaminated sites [6,7]. Based on the field experiences, remedial costs of MTBE-impacted sites could be 100–200% more than typical BTEX sites [3].

Natural attenuation (NA) is a passive and cost-effective remedial approach that depends upon natural processes to degrade and dissipate contaminants in soil and groundwater. Natural biotic and abiotic mechanisms such as dispersion, sorption, volatilization, dilution, abiotic degradation, and biodegradation are responsible for the decrease of mass, toxicity, volume, concentrations, and mobility of contaminants in soil or groundwater. For petroleum-contaminated sites, intrinsic biodegradation is the most important process to the destruction of contaminants. However, other nondestructive mechanisms are also important because they may result in a decrease in contaminant concentration especially in the contaminated sites that have low biodegrading potential. Although no active human intervention are applied to this technology, it does not mean that natural attenuation is a "no action" approach. Long-term monitoring should be taken to verify the decrease and containment of the plume to protect residents and environment in the downgradient area. Consequently, the term "monitored natural attenuation" (MNA) is more appropriate for this technology [8–10].

Although the properties of MTBE may increase the difficulty of the use of natural attenuation [11], evidences and some successful cases of MTBE attenuation have been reported that make natural attenuation as a considerable remedial strategy [10,12–14]. Wilson and Kolhatkar [15] evaluated MTBE attenuation of five sites and suggested that MTBE at all sites could be controlled by the natural attenuation processes. The first-order attenuation rates in the plumes varied from 0.56 to 4.3 year⁻¹. Borden et al. [16] have reported that MTBE was reduced near the contaminant source at a petroleum-hydrocarbon contaminated site. However, there was no significant MTBE reduction in the downgradient area. The biodegrading rate of MTBE varied from 0 to 0.001 day⁻¹. Recent field investigations also indicate that natural biodegradation of MTBE may occur under both aerobic and anaerobic subsurface environment [14,17]. However, if the rate of MTBE biodegradation is not significant enough to contain the plume, natural attenuation will not be sufficient to protect aquifers and downgradient receptors [18].

In this study, two petroleum-hydrocarbon contaminated sites (Sites A and B) containing significant amount of MTBE were selected to assess the occurrence and effectiveness of

natural attenuation of MTBE. Groundwater sampling and analyses were implemented to obtain the evidences of natural attenuation. A natural attenuation model, BIOSCREEN [19], was applied to simulate the effectiveness and first-order rates of natural attenuation. The main objectives of this study were to: (1) evaluate the occurrence and effectiveness of natural attenuation, (2) assess the feasibility of using natural attenuation to control the MTBE plume, and (3) evaluate the contributions of intrinsic biodegradation patterns on natural attenuation processes.

2. Site description

The two sites selected for this MNA study are located in southern Taiwan. Site A is an oil-refining plant, which produces gasoline, diesel, jet fuel, kerosene, and lubricating oils. Inappropriate operation has resulted in the generation of BTEX and MTBE plumes. Results from previous studies reveal that the highest MTBE and BTEX concentrations were about 145 and 200 mg/L in collected groundwater samples, respectively [20]. The edge of MTBE plume was approximate 640 m downgradient from the spill location. Soils at Site A consist of silty sand, silt, and clay, and the main component of site soils is silty sand. A thickness of 5–10 m weak clay layer is located at 40 m below land surface. The groundwater flows as a velocity of 0.2–1.4 m/day from southwest to northeast. According to the results from hydrogeologic tests, the average hydraulic conductivity of the host geological material is 0.05 cm/s, and the groundwater slope is approximately 0.25% [20]. Fig. 1 presents the site map of Site A showing the contaminant source area, estimated MTBE plume, and the monitor wells used in this study.

Site B is an oil tank farm where gasoline, diesel, jet fuel, kerosene, and lubricating oils are stored. Contamination of groundwater has occurred due to the leakage of pipeline and has resulted in concentrations of 265 µg/L of MTBE and 1.2 mg/L of BTEX at highly contaminated zone. The MTBE plume was approximate 280 m. The main components of soils are silty sand and silt clay at Site B. The groundwater flows from northeast to southwest as a velocity 0.03 m/day. The measured average hydraulic conductivity is 0.003 cm/s, and the groundwater slope is approximately 0.38% [21]. Fig. 2 presents the site map of Site B showing the contaminant source area, estimated MTBE plume, and the monitor wells used in this study.

3. Materials and methods

Monitor wells located along the centerline of the plume were selected to monitor the concentrations of contaminants in the source zone, mid-gradient, and downgradient of the plume. In addition, a monitor well at upgradient area was selected to obtain background information at each site. All selected wells at both sites were sampled quarterly during

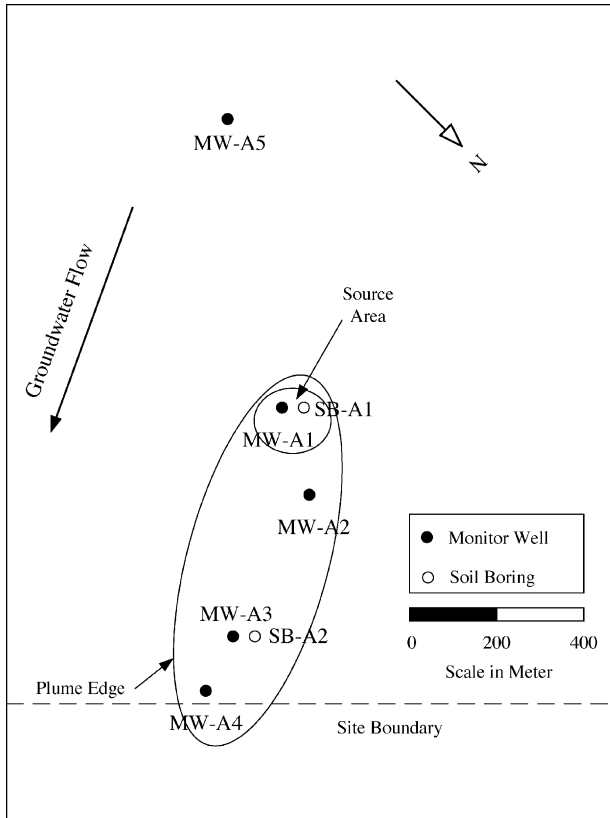


Fig. 1. Site map showing the contaminant source area, estimated MTBE plume, and the monitor wells at Site A.

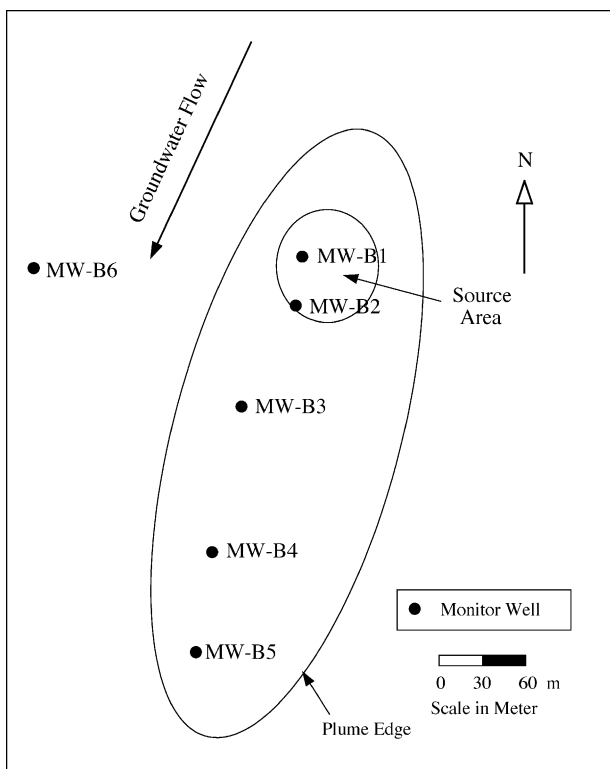


Fig. 2. Site map showing the contaminant source area, estimated MTBE plume, and the monitor wells at Site B.

the 2-year investigation period. Thus, the data presented in this study are averaged results for eight sampling events. Prior to the sampling process, the headspace of all monitoring wells were filled with argon gas to prevent oxygen intrusion. A minimum of three to five well volumes of well water were purged by a submersible pump. Groundwater samples were collected from monitoring wells by bailers after the well purging process. The collected samples were transported to the laboratory on ice and then stored at 4 °C before the analysis. Samples were analyzed for organic compounds and geochemical indicators including MTBE, TBA, BTEX, methane (CH₄), carbon dioxide (CO₂), anions, and dissolved oxygen (DO). Organic compound analyses were performed in accordance with US EPA Method 502.2, using a Varian 3800 gas chromatograph (GC). Because TBA is the byproduct of MTBE biodegradation, TBA was analyzed in this study for the evaluation of intrinsic biodegradation process.

The analysis of methane was performed with a Shimadzu GC-9A GC using headspace techniques. Ion chromatography (Dionex) was used for anions (NO₃⁻, SO₄²⁻) analyses. Total iron, ferrous, and sulfide were analyzed by Hach DR/400 Spectrophotometer using EPA Method 8008, Method 8146, and Method 8131, respectively. DO, pH, and CO₂ were measured in the field. A WTW DO meter (Oxi 330) was used for DO measurements, pH was measured by a Mettler Toledo pH meter (MP120), and a Hach digital titrator cartridge was used for CO₂ measurements.

Aquifer sediments at depth from 3.8 to 4.5 m were collected by a Geoprobe™ direct push system. Aquifer sediments from the soil boring SB-A1 and SB-A2, and groundwater collected from MW-B1 and MW-B6 were used to determine the number of total heterotrophs. Total plate counts were conducted using plate count agar (Difco) to assess the approximate population of the total heterotrophic bacterial in soil or groundwater samples using the spread plate method [22]. Prepared plates were incubated at 30 °C for 48 h, then counted for colony forming unit (CFU).

In this study, BIOSCREEN model was used to evaluate the percent loss of MTBE due to the biodegradation and to simulate the possible extent of MTBE plumes. BIOSCREEN has the ability to simulate variations of a contaminated plume with time [19]. Hydrogeologic and biological factors of sites are considered in this model to obtain reasonable results. Biodegradation of contaminants can be described as a first-order process or instantaneous reaction with electron acceptors. Because MTBE is a more persistent compound, instantaneous reaction model is not suitable to use [19]. Thus, the first-order decay model was selected to simulate MTBE biodegradation. An infinite source was assumed to simulate the most serious condition due to the source mass were unavailable at both sites. In this study, 15 and 8 years were selected as the simulation periods, respectively, according to the historical data of Sites A and B. The values of the major parameters used in BIOSCREEN are listed in Table 1.

Table 1
The major parameters used in BIOCSREEN

| Data type | Parameter | Site A | Site B | |
|---------------------|--|-------------------------------|----------|------|
| Hydrogeologic data | Seepage velocity (m/year) | 292.0 | 11.7 | |
| | Dispersion | Longitudinal dispersivity (m) | 10.7 | 34.4 |
| | | Transverse dispersivity (m) | 1.1 | 3.4 |
| | | Estimated plume length (m) | 762 | 305 |
| Biodegradation data | Solute half-life (year) | 1.2 | 1.2 | |
| | General data | Modeled area length (m) | 2286 | 345 |
| | | Modeled area width (m) | 305 | 183 |
| | | Simulation time (year) | 15 | 8 |
| Source data | Source thickness in saturated zone (m) | 6.1 | 6.1 | |
| | Source concentration (mg/L) | 0.2 | 0.25 | |
| | Soluble mass in source (kg) | Infinite | Infinite | |

4. Results and discussion

Groundwater samples collected from the two studied sites were analyzed for organic compounds and geochemical indicators to evaluate the occurrence of natural attenuation of MTBE. Tables 2 and 3 show the averaged results of groundwater analyses of Sites A and B, respectively. The concentrations of MTBE were reduced along groundwater flow from source zones to downgradient areas at both Site A (207–51 $\mu\text{g/L}$) and Site B (110–3 $\mu\text{g/L}$). Figs. 3 and 4 show the MTBE and TBA concentrations versus distance to spill location at Sites A and B, respectively. Note that the concentrations of MTBE increased from MW-B1 to MW-B2, this variation might be due to storms or the former pumping task. Investigating results reveal that the decreases of MTBE at the two sites were significant. The contribution of natural attenuation can be expressed as a first-order decay process [15]. The rates of MTBE natural attenuation calculated from the

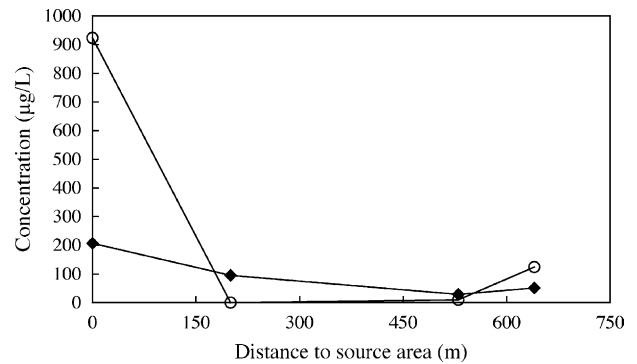


Fig. 3. MTBE and TBA concentrations vs. distance to spill location at Site A: (◆) MTBE; (○) TBA.

Table 2
Field investigation results of Site A

| | MW-A1 | MW-A2 | MW-A3 | MW-A4 | MW-A5 | SB-A1 | SB-A2 |
|-----------------------------|--|--------------------|-------------------|-------------------|-------------------|------------------------------|------------------------------|
| Distance to source zone (m) | 0 | 200 | 530 | 640 | ^a | – | – |
| MTBE ($\mu\text{g/L}$) | 207 ^b \pm 68 ^c | 95 \pm 33 | 29 \pm 15 | 51 \pm 20 | 0 | – | – |
| TBA ($\mu\text{g/L}$) | 923 \pm 221 | 0 | 10 \pm 7 | 124 \pm 52 | 0 | – | – |
| Benzene (mg/L) | 58.354 \pm 22.329 | 9.530 \pm 3.261 | 0.259 \pm 0.132 | 0.188 \pm 0.064 | 0 | – | – |
| Toluene (mg/L) | 28.917 \pm 10.267 | 0.684 \pm 0.040 | 0.218 \pm 0.099 | 0.072 \pm 0.037 | 0 | – | – |
| Ethylbenzene (mg/L) | 8.648 \pm 3.549 | 0.066 \pm 0.312 | 0.055 \pm 0.021 | 0.035 \pm 0.020 | 0 | – | – |
| Xylenes (mg/L) | 10.428 \pm 5.024 | 0.862 \pm 0.297 | 0.186 \pm 0.045 | 0.107 \pm 0.043 | 0 | – | – |
| Total BTEX (mg/L) | 106.346 \pm 34.264 | 11.143 \pm 4.241 | 0.717 \pm 0.325 | 0.403 \pm 0.197 | 0 | – | – |
| pH | 6.73 \pm 0.21 | 6.74 \pm 0.09 | 7.07 \pm 0.12 | 6.71 \pm 0.11 | 6.64 \pm 0.17 | – | – |
| DO (mg/L) | 0.33 \pm 0.11 | 0.37 \pm 0.07 | 0.41 \pm 0.15 | 0.36 \pm 0.11 | 2.10 \pm 1.02 | – | – |
| Nitrate (mg/L) | 0.19 \pm 0.06 | 0.11 \pm 0.09 | 0.12 \pm 0.03 | 0.28 \pm 0.11 | 1.12 \pm 0.10 | – | – |
| Total iron (mg/L) | 9.82 \pm 2.73 | 9.19 \pm 2.33 | 3.82 \pm 1.14 | 7.75 \pm 1.69 | 2.07 \pm 0.88 | – | – |
| Ferrous iron (mg/L) | 7.89 \pm 2.28 | 6.50 \pm 2.80 | 2.71 \pm 1.13 | 5.92 \pm 1.57 | 0.97 \pm 0.40 | – | – |
| Sulfate (mg/L) | 4.24 \pm 1.56 | 17.40 \pm 4.28 | 15.67 \pm 5.33 | 5.77 \pm 2.24 | 23.66 \pm 9.32 | – | – |
| Sulfide ($\mu\text{g/L}$) | 45 \pm 20 | 145 \pm 32 | 109 \pm 17 | 15 \pm 9 | 68 \pm 16 | – | – |
| Carbon dioxide (mg/L) | 249 \pm 40 | 131 \pm 29 | 102 \pm 24 | 244 \pm 53 | 51 \pm 18 | – | – |
| Methane (mg/L) | 8.130 \pm 2.36 | 7.260 \pm 3.254 | 3.160 \pm 1.015 | 3.130 \pm 0.846 | 0.030 \pm 0.011 | – | – |
| Total heterotrophs (CFU/g) | – | – | – | – | – | 1.2 \times 10 ⁶ | 3.0 \times 10 ⁷ |

“–” not available.

^a Background monitor well.

^b Arithmetic mean.

^c Standard deviation.

Table 3
Field investigation results of Site B

| | MW-B1 | MW-B2 | MW-B3 | MW-B4 | MW-B5 | MW-B6 |
|-----------------------------|--|-------------------|-------------------|-------------------|-------------------|------------------------------|
| Distance to source zone (m) | 0 | 30 | 100 | 210 | 280 | ^a |
| MTBE ($\mu\text{g/L}$) | 110 ^b \pm 41 ^c | 265 \pm 87 | 4 \pm 1 | 4 \pm 2 | 3 \pm 2 | 0 |
| TBA ($\mu\text{g/L}$) | 387 \pm 112 | 1020 \pm 357 | 152 \pm 48 | 0 | 0 | 0 |
| Benzene | 0.141 \pm 0.024 | 0.295 \pm 0.117 | 0.035 \pm 0.011 | 0.001 \pm 0.001 | 0 | 0 |
| Toluene | 0.170 \pm 0.035 | 0.204 \pm 0.009 | 0.002 \pm 0.001 | 0 | 0 | 0 |
| Ethylbenzene | 0.105 \pm 0.019 | 0.791 \pm 0.265 | 0.009 \pm 0.002 | 0 | 0 | 0 |
| Xylenes | 0.237 \pm 0.077 | 0.294 \pm 0.035 | 0.002 \pm 0.001 | 0 | 0 | 0 |
| Total BTEX (mg/L) | 0.653 \pm 145 | 1.208 \pm 376 | 0.047 \pm 0.017 | 0.001 \pm 0.001 | 0 | 0 |
| pH | 6.70 \pm 0.11 | 6.73 \pm 0.09 | 7.12 \pm 0.04 | 6.63 \pm 0.10 | 6.80 \pm 0.07 | 6.88 \pm 0.13 |
| DO (mg/L) | 0.5 \pm 0.2 | 0.4 \pm 0.1 | 1.4 \pm 0.5 | 1.5 \pm 0.3 | 1.3 \pm 0.2 | 2.4 \pm 0.7 |
| Nitrate (mg/L) | 0.2 \pm 0.1 | 0.8 \pm 0.3 | 37.6 \pm 10.7 | 41.3 \pm 12.1 | 13.3 \pm 5.3 | 83.4 \pm 27.2 |
| Total iron (mg/L) | 18.4 \pm 6.9 | 30.9 \pm 12.3 | 1.7 \pm 0.4 | 2.0 \pm 0.6 | 2.9 \pm 1.1 | 1.74 \pm 0.25 |
| Ferrous iron (mg/L) | 11.7 \pm 4.7 | 9.4 \pm 4.2 | 0.1 \pm 0.1 | 0.04 \pm 0.01 | 0.2 \pm 0.1 | 0.2 \pm 0.1 |
| Sulfate (mg/L) | 10.1 \pm 3.1 | 58.4 \pm 23.1 | 69.4 \pm 23.3 | 37.8 \pm 15.6 | 108.7 \pm 37.2 | 102.2 \pm 32.7 |
| Sulfide ($\mu\text{g/L}$) | 17 \pm 7 | 34 \pm 15 | 11 \pm 5 | 6 \pm 2 | 7 \pm 2 | 10 \pm 4 |
| Carbon dioxide (mg/L) | 250 \pm 83 | 252 \pm 102 | 177 \pm 73 | 179 \pm 44 | 180 \pm 78 | 167 \pm 68 |
| Methane (mg/L) | 2.101 \pm 0.634 | 3.623 \pm 1.213 | 0.056 \pm 0.009 | 0.010 \pm 0.002 | 0.008 \pm 0.003 | 0.002 \pm 0.001 |
| Total heterotrophs (CFU/mL) | 1.0 \times 10 ³ | – | – | – | – | 1.6 \times 10 ³ |

“–” not available.

^a Background monitor well.

^b Arithmetic mean.

^c Standard deviation.

sites were 0.0021 and 0.0048 day⁻¹ at Sites A and B, respectively. In addition, the calculated decay rates for BTEX were 0.0087 and 0.0339 day⁻¹ at Sites A and B, respectively. The results indicate that BTEX had more effective decay rates than MTBE.

In general, the direct evidence of contaminant biodegradation would be the production of degradation byproducts. At both sites, TBA, the byproduct of MTBE biodegradation, was detected. The highest concentrations were 923 and 1020 $\mu\text{g/L}$ at Sites A and B, respectively. Production of TBA indicates that intrinsic biodegradation had significant contributions to MTBE consumption within the plumes. The anoxic conditions of source zones at both sites suggest that MTBE was biodegraded anaerobically. Although a slight accumulation of TBA was detected at source zones of both sites (Figs. 3 and 4), significant drops of TBA concentrations were also observed in the mid and downgradient areas. This

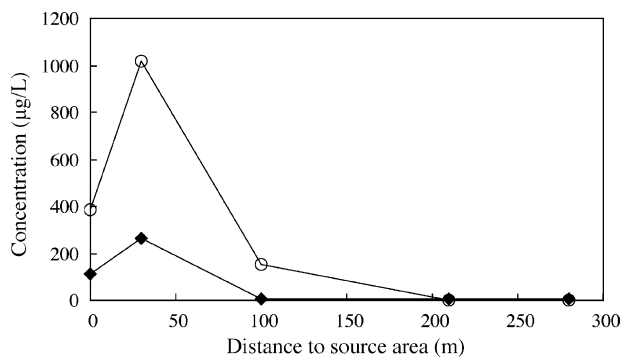


Fig. 4. MTBE and TBA concentrations vs. distance to spill location at Site B: (◆) MTBE; (○) TBA.

indicates that TBA was also degraded under the natural attenuation processes.

Results from our previous laboratory microcosm study (inoculated with aquifer sediments from Site A) suggest that MTBE could only be biodegraded aerobically [23]. This might be due to the variation in the environmental conditions between laboratory and field. Consequently, the laboratory results should be explained more carefully to prevent misleading conclusions.

Results from our previous study indicate that the presence of BTEX is able to enhance the biodegradation of MTBE [24]. However, no significant relationship between removal of BTEX and MTBE could be obtained from the field data. Lower MTBE removal rates were observed in the downgradient area of the plumes compared to the rates near the source areas. Thus, the dilution and dispersion processes might be the major mechanisms, which are responsible for the attenuation of MTBE in the downgradient areas.

Other evidences of distinct microbial activities were also observed. A significant amount of total heterotrophs ($>10^6$ CFU/g of soil) were detected in the collected SB-A1 and SB-A2 samples at Site A. Total heterotrophs in groundwater samples MW-B1 and MW-B6 were about 10^3 CFU/mL of groundwater at Site B. Low DO and high CO_2 within both plumes suggest that aerobic biodegradation occurred at both sites and caused the depletion of DO and production of CO_2 . High methane concentrations were detected in the collected groundwater samples near source zones at Site A and Site B. Thus, methanogenesis might be the dominant biodegradation pattern within the contaminated zones.

Compared to the background monitor wells (MW-A5 and MW-B6), higher ratios of ferrous to total iron concentrations

and lower nitrate and sulfate concentrations were detected near the source zones. This indicates that nitrate, ferric iron, and sulfate might have been used as the electron acceptors at both sites after the depletion of oxygen. DO concentrations in the monitor wells MW-B3, MW-B4, and MW-B5 at Site B were greater than 1 mg/L. This suggests that the dominant biological mechanism within the downgradient area of the plume at Site B was aerobic biodegradation. This was confirmed by the low ferrous iron and methane concentrations in the downgradient area. Results from the field investigation suggest that the consumption of various electronic acceptors and production of their byproducts were significant within the plumes at both sites. These findings suggest that the indigenous microorganisms were active under both aerobic and anaerobic site conditions. Thus, intrinsic biodegradation played an important role on contaminant removal at both sites.

In this study, MTBE concentration of 20 $\mu\text{g/L}$ was used as the remediation goal based on the advisory of the US EPA [1]. Results from field investigation of Site B show that only 3 $\mu\text{g/L}$ MTBE and no BTEX were observed in MW-B5. Thus, it is feasible to control the MTBE and BTEX plumes using the natural attenuation mechanisms at Site B. However, significant MTBE (51 $\mu\text{g/L}$) and BTEX (403 $\mu\text{g/L}$) concentrations were observed in MW-A4 at Site A, which is very close to the site boundary. Although obvious microbial activities and natural attenuation processes are occurring, the contaminants could not be effectively contained within the Site A boundary. Results suggest that more active groundwater remedial technologies should be applied at Site A to protect the down-gradient environment.

The BIOSCREEN model was used in this study to evaluate the contributions of intrinsic biodegradation on natural attenuation. Modeling results show that the MTBE plume would contain 98.4 kg of MTBE at Site A if biodegradation processes did not occur in the plume. Results indicate that a significant amount of MTBE was biodegraded via mixed intrinsic biodegradation patterns, and only 21.6 kg of MTBE remained within the plume. Thus, approximately 78% of MTBE mass at Site A was removed due to the biological processes. Results reveal that the mass of MTBE at Site B dropped from 1.7 to 0.7 kg due to the occurrence of biodegradation mechanisms. Thus, 59% of MTBE mass was removed as a result of the intrinsic biodegradation. Figs. 5 and 6 show the simulated and actual MTBE concentrations along the centerlines at Sites A and B. The first-order decay model was applied in the modeling task. The simulated results reveal that MTBE at Site A would transport more than 900 m from the source before its concentration drops to below 20 $\mu\text{g/L}$ (Fig. 5). In other words, MTBE would exceed the site boundary in a distance of about 280 m before the advisory concentration is reached. This gives us a preliminary suggestion that a more aggressive remedial action is required at this site. In addition, the distinct contribution of biodegradation could also be observed in Fig. 5 compared to the simulated results with no degradation model. As shown in Fig. 6, MTBE could

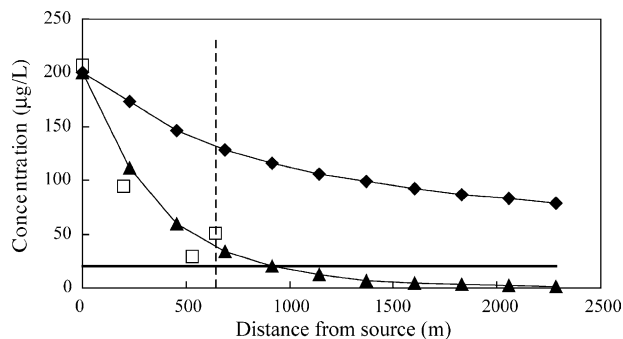


Fig. 5. The simulated and actual MTBE concentrations along the centerline at Site A: (◆) no degradation; (▲) first-order decay; (□) field data from site; (—) criteria; (---) site boundary.

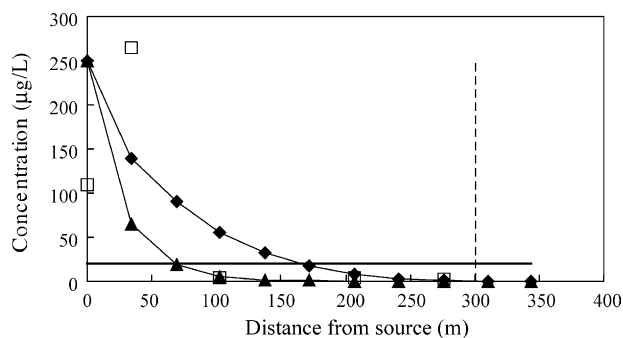


Fig. 6. The simulated and actual MTBE concentrations along the centerline at Site B: (◆) no degradation; (▲) first-order decay; (□) field data from site; (—) criteria; (---) site boundary.

be contained within the site boundary at the time of simulation (8 years) with or without the occurrence of biodegradation. However, the containment will be ineffective after 15 years if biological process was not occurring (data not shown). This also reveals that intrinsic biodegradation is the most important mechanism among those natural attenuation processes.

5. Conclusions

In this study, the natural attenuation of MTBE was evaluated at two petroleum-hydrocarbon contaminated sites. Field investigation results show that natural attenuation of MTBE was occurring with rates of 0.0021 and 0.0048 day^{-1} at Sites A and B, respectively. Evidences of intrinsic biodegradation include the following:

- (1) depletion of DO, nitrate, and sulfate within the plume;
- (2) production of dissolved ferrous iron, sulfide, methane, and CO_2 within the plume;
- (3) decreased MTBE concentrations along the transport path,
- (4) increased microbial populations;
- (5) accumulation of MTBE biodegradation byproduct (TBA).

Production of TBA within the anaerobic source zone also reveals that the anaerobic MTBE biodegradation might be occurring at both sites. Moreover, aerobic biodegradation might be the dominant biological mechanism in the down-gradient area of the plume at Site B. However, anaerobic processes might dominate the entire plume at Site A. Results from BIOSCREEN simulation suggest that biodegradation was responsible for 78% and 59% of MTBE mass reduction at Sites A and B, respectively.

Although significant microbial activities were observed, the contaminants could not be contained inside the boundary at Site A. BIOSCREEN results show that MTBE would exceed the site boundary in a distance of 280 m before the advisory concentration 20 µg/L is reached. Thus, more active technologies should be applied to protect the down-gradient environment. Enhanced bioremediation or pump and treat systems might be applied to further contain the plume.

Based on the results from the field investigation, natural attenuation of MTBE was occurring at both sites. The intrinsic biodegradation had significant contributions on the control of MTBE plumes. However, results also reveal that intrinsic biological processes might still fail to contain the plume if the selected point of compliance is not appropriate. Investigation results show that MTBE plume at Site B could be effectively controlled via natural attenuation processes. However, MTBE plume at Site A has migrated to a farther downgradient area and passed the boundary of the site. Thus, it is necessary to implement a detailed field investigation to assure the effectiveness of natural attenuation before it is applied as the remedial option at the MTBE-contaminated sites.

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