

NATURAL ATTENUATION OF MTBE

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ABSTRACT

Three case studies of MTBE contamination of ground water are presented. Each study site had its own unique geochemical characteristics. At the first study site dissolved oxygen was the dominant electron acceptor. At the second site, the dominant electron acceptors were methanogenesis and iron reduction. At the third site, the dominant electron acceptor was sulfate reduction. At the first site, the total mass of BTEX compounds decreased over three rounds of sampling, indicating a net loss of mass in the aquifer. In contrast, the MTBE data did not show a clear trend of attenuation over time. Under methanogenic conditions at the second site, the distribution of MTBE in the plume provided evidence of natural attenuation of MTBE in the ground water. A mass balance analysis evaluated the rate of natural attenuation of the source area. Under sulfate reducing conditions at the third site, there was field scale evidence of natural attenuation, but attenuation may have resulted from physical processes such as dilution and dispersion, and not through natural biodegradation. Although the rate of attenuation of MTBE was not fast compared to attenuation of BTEX compounds, the rate was of environmental significance, and it could be estimated qualitatively.

1. INTRODUCTION

Methyl tert-butyl ether (MTBE) has been added to gasoline since the 1970s. Initially, MTBE was added as an octane-enhancing replacement for tetraethyl lead, which was being phased out of use. Later, MTBE was used as a fuel oxygenate to decrease the amount of carbon monoxide in automobile emissions. The 1990 Clean Air Act amendment mandated the seasonal use of fuel oxygenates, such as MTBE, in certain parts of the United States. This use has resulted in MTBE being released to ground water (Squillace et al. [1]). Initial research on MTBE indicated that it was relatively recalcitrant to biodegradation. Later, evidence began to emerge showing that MTBE was biodegradable under certain conditions or when certain microorganisms were present. Biodegradation under aerobic conditions was reported in several papers (Salanitro et al. [2,3], Mo et al. [4]). Park and Cowan [5] reported aerobic biodegradation with a half-life of MTBE about 2 days for selected microorganisms in the laboratory. Field studies of MTBE biodegradation (Borden et al. [6], Landmeyer et al. [7]) indicated that under certain anaerobic conditions, MTBE biodegradation with low but measurable rates occurred. Mormile et al. [8] and Yeh and Novak [9] reported limited biodegradation under anaerobic conditions.

The current consensus of research is that MTBE is biodegradable, but rates are low relative to BTEX compounds (Chapelle [10]). This has shown that intrinsic biodegradation is less efficient for MTBE than it is for BTEX compounds. Because of its high solubility, low adsorption on soil, and very limited biodegradation rate, the sizes of MTBE plumes in groundwater are much larger than BTEX plumes.

In this paper, we present three case studies of natural attenuation of MTBE in ground water. The first case study was conducted at a gas station site in Long Island, New York. The MTBE plume distribution was controlled by geochemical changes in the aquifer caused by previous releases of BTEX compounds. Previous releases of BTEX had depleted the oxygen in the aquifer. The plume MTBE was contained within a region

of aquifer that had been previously depleted of oxygen, and as a consequence, no oxygen was available for aerobic metabolism of MTBE. The MTBE could be thought to be hiding behind the shadow of depleted dissolved oxygen. The natural attenuation of MTBE was evidenced from decreasing MTBE mass in historical monitoring data. This case was the work of the US EPA and New York State Department of Environmental Quality.

The second case is the US EPA and US Coast Guard's work in the US Coast Guard Supply Center, North Carolina. The geochemical condition was methanogenic. The source of the plume was from the old fuel tank farm. We approached this site with mass balance analysis. Third case is the US EPA's work at the gasoline spill site from the service station in the US Navy base, California. Several studies on the MTBE plume are still ongoing at the site, including active bioremediation, soil venting and air sparging, phytoremediation, and natural attenuation. The EPA researchers are conducting a natural attenuation study in the field and a laboratory microcosm study. The dominant biodegradation processes for BTEX and MTBE at the site were iron reduction and methanogenesis. A preliminary analysis of field data showed that MTBE concentrations in the plume along the center path were declining.

2. CASE 1: SERVICE STATION IN LONG ISLAND, NEW YORK

Subsurface contamination was detected at E. Patchogue, New York when water from a residential well became undrinkable. The drinking water was rendered undrinkable because of high concentrations of methyl *tert*-butyl ether (MTBE). Later sampling also found high concentrations of benzene, toluene, ethyl benzene and xylene isomers (BTEX) from locations near this well. By sampling, the State traced the contamination back toward an abandoned service station approximately 4000 feet (1200 m) up gradient from the contaminated well. Soil borings in the area of the service station confirmed the presence of hydrocarbon contamination. The tanks in the service station were probably removed in 1988, which could be the latest date that gasoline could have been released.

This gasoline spill was an unusual case study because of the size of the contaminant plume and because of the relatively large amount of data available from the site. Data from multilevel samplers and screened wells were used to delineate the extent of BTEX and MTBE contamination. The contaminant plume was found to extend from the suspected source down gradient toward the shoreline of Great South Bay, which is located just south of the site (Figure 1). In 1994 and 1995, the contaminant plume was mapped from samples taken from 26 multilevel samplers and 22 monitoring wells. Water samples from four sampling rounds were analyzed for BTEX and MTBE. Total organic carbon contents were determined on 11 clean core samples.

Published studies of groundwater flow on Long Island indicated that a regional ground water divide lies along the length of the island and to the north of the geographic centerline (Eckhardt and Stackelberg [11]). South of the divide, flow is generally toward the Atlantic Ocean. Buxton and Modica [12] estimated that the hydraulic conductivity of the upper glacial aquifer is on the order of 8.1×10^{-4} cm/sec (230 ft/day) in the outwash section near the southern shore, with estimated ground water velocity of 110 meters per year (360 ft/year) or greater.

Moments Analysis

The relatively large number of monitoring wells and multilevel samplers generated a three-dimensional data set, which were analyzed by calculating the spatial moments of each concentration distribution. For most of the plume, the wells crossed the entire width of the plume. In some locations, however, monitoring wells with high contaminant concentrations were located on the edge of the sampling network. Therefore some of the contaminant mass was not included in the estimates given below. Because the MTBE plume was located down-gradient of MW-30, MW-38, and MW-39, the MTBE plume was contained within the sampling network, and the mass estimates of MTBE were not greatly impacted by the spacing of monitoring wells.

Table 1 shows the mass estimates and the distance of the center of mass of BTEX and MTBE from the source. Data in sampling round one were taken as the wells were installed from July 1994 to March 1995. Data from sampling round two were taken from April 11, 1995 to April 20, 1995 and those from sampling round three were taken from October 10, 1995 to October 24, 1995. Since the sampling in round one was done over a long time period, contaminants sampled up-gradient may have been transported to down-gradient receptor wells before they were sampled.

The porosity and solids density were assumed to be 0.30 and 2.65 g/cm³, respectively, giving a bulk density of 1.86 g/cm³. Table 1 lists estimated sorbed masses for each chemical. The estimated mass of BTEX compounds decreased between each sample round. Each of these compounds was expected to undergo biodegradation in the aquifer, but each continued to dissolve into the aquifer through October 1995. The latter fact was established by the persistence of BTEX concentrations near the source. The mass of MTBE, however, appeared to increase between the first two sample rounds; then decreased between the second and third sample rounds. MTBE was not detected between the source and a point approximately 600 m (2000 ft) down-gradient (Figure 2). Thus it appeared that MTBE was almost entirely leached from the gasoline near the source.

MTBE and Electron Acceptors Distribution

The most interesting and unique characteristic of the MTBE plume at this site is the fact that MTBE was distributed along the low concentration zone of dissolved oxygen. Comparing the MTBE plume (Figure 2) and dissolved oxygen distribution (Figure 3) reveals that the MTBE plume located where the dissolved oxygen concentration was less than 2 mg/L. Geochemical analysis of the ground water indicated that the ground water at the site had very low levels of nitrate, iron II, and methane. Sulfate concentration was generally high (more than 30 mg/L) and the sulfate was not being used as the primary electron acceptor inside the MTBE plume. At this site, the major electron acceptor used for hydrocarbon degradation was the dissolved oxygen.

**Table 1. Moment Based Mass Estimates and Center of Mass (E. Patchogue, NY)
From Weaver et al. [13]**

	Sample Round 1			Sample Round 2			Sample Round 3		
	M_w (kg)	M_s (kg)	d (m)	M_w (kg)	M_s (kg)	d (m)	M_w (kg)	M_s (kg)	d (m)
MTBE	268	24	1387	386	34	1557	229	20	1583

B	241	156	991	117	76	1004	58	38	1061
T	108	253	230	65	152	298	60	141	306
E	29	249	347	24	206	347	21	180	326
X	149	1041	222	95	663	277	92	643	272

M_w : Mass dissolved in ground water

M_s : Mass sorbed to the solid, estimated from K_{oc}

d : distance of the center of mass from the suspected source

3. CASE 2: US COAST GUARD SUPPORT CENTER, ELIZABETH CITY, NORTH CAROLINA

This study was conducted at the former fuel farm site at the US Coast Guard Support Center, Elizabeth City, North Carolina. The following description is excerpted from the Former Fuel Farm Work Plan, a part of the Remediation Feasibility Assessment Work Plan prepared for the U.S. Coast Guard Support Center Elizabeth City, North Carolina, by Parsons Engineering Science, 1996.

The Support Center is located on the southern bank of the Pasquotank River. The former fuel farm was located south of concrete ramp used to recover seaplanes from the river (Figure 4). Currently a plume of MTBE and fuel hydrocarbons in ground water emanates from a source area in the location of the former fuel farm, and flows under the concrete ramp toward the river to the North, and toward a drainage canal along the western side of the seaplane ramp. This source area corresponds to the former location of fuel storage tanks on the site.

The fuel farm had been in use since 1942, and originally consisted of a 50,000-gallons (190,000 liter) concrete underground storage tank and two steel underground storage tanks with a volume of 12,000-gallons (45,000 liter) and 15,000-gallons (57,000 liter) respectively (Adjacent to location CPT-1 in Figure 4). The steel tanks were apparently removed in mid 1980s. In addition to the underground storage tanks, two steel above ground storage tanks with a capacity of 50,000 gallons (190,000 liters) were installed in mid 1980s. There was evidence of corrosion in the transfer lines from these tanks. They were taken out of service and removed from the site. No evidence of a release from the pipes was discovered.

The U.S. Coast Guard began a free product recovery effort at the site in September 1990. Eight recovery wells were arranged around the source area in a circle. By March 1992, a total of 79,000 gallons (300,000 liters) of fuel was recovered.

Core Sampling in Source Area

In September 1996, a Geoprobe™ direct push system was used to acquire core samples in continuous vertical profiles at seven locations in or near the source. The water table was detected at the depth 7.0 to 8.0 feet (2.1 to 2.4 meters) below land surface. The cores extended from the surface to a depth 12 to 16 feet (3.7 to 4.9 meters).

The cores were cut into subcores of 4 inches (10 cm) length and a plug was acquired from each subcore ~~was~~ extracted with 10 ml of methylene chloride and 5 ml of distilled water. Those samples were shipped to the laboratory for analysis by a GC/MS.

The cores at each sampling location extended from clean soil above the release, through the release to clean aquifer material below the release. The quantity of Total Petroleum Hydrocarbon (TPH) or MTBE in individual cores was summed to determine the total amount of TPH and MTBE present at each location. The greatest quantity of TPH was found at locations CPT-2 and CPT-1 (Figure 4). These locations were near the location of the original underground storage tanks. These two locations also had the greatest mass of MTBE. The fuel release that contains MTBE is centered around locations CPT-1 and CPT-2. With the assumed source area of 11,000 m², the total quantity of fuel hydrocarbons remaining in the source was estimated to be about 500,000 kg. With the fuel density of 0.82 kg/liter, this corresponds to 620,000 liters (180,000 gallons) of fuel. The total quantity of MTBE was estimated to be in the range of between 46 kg and 140 kg.

Geochemical Context of the MTBE Plume

The MTBE plume was contained within a plume of methane. Methane concentrations generally exceeded 3.0 mg/liter, and often exceeded 10 mg/liter. In general, this aquifer was strongly methanogenic. Concentrations of methane averaged 7 mg/liter, which corresponds to 9 mg/liter of hydrocarbon originally metabolized. Approximately 6 mg of carbon dioxide would also be produced (Wiedemeier et al. [14]). The MTBE plume and BTEX plume were contained within a region of the aquifer that is depleted of molecular oxygen. Many regions of the aquifer had less than 0.1 mg/liter oxygen. The background concentration of dissolved oxygen was near 3.6 mg/liter. Ground water in the region of the aquifer that contains MTBE and BTEX compounds was also depleted of sulfate. Sulfate concentrations were reduced from a background of near 28 mg/liter to less than 4 mg/liter. The same regions that were depleted in molecular oxygen and sulfate had significant accumulations of Iron II. The background concentration of Iron II was less than 1 mg/liter. Many regions of the aquifer with MTBE and BTEX compounds had Iron II concentrations greater than 50 mg/liter. The pH of the plume was generally near 6.5 and below 6.0 only in the ground water that was in direct contact with the LNAPL. Under these conditions, carbon dioxide produced through oxidation of petroleum hydrocarbons would react with carbonate minerals in the aquifer matrix to produce bicarbonate alkalinity in the ground water. Data showed that as much as 200 mg/liter of alkalinity was produced by oxidation of petroleum hydrocarbons. This corresponds to 88 mg/liter of carbon dioxide produced or 28 mg/liter of TPH consumed. There was more than enough carbon dioxide production to account for the depletion of oxygen and sulfate, and the production of Iron II and methane.

Calculation of Mass Transfer of MTBE from the Entire Source Area to the Plume

The mass transfer of MTBE from the source LNAPL to the ground water moving underneath was estimated by calculating the flux of MTBE moving away from the source across the East-West transect (A-A* in Figure 4), then comparing that flux to the total mass of MTBE in the source area.

The average hydraulic conductivity for the site was used to calculate the Darcy's velocity that corresponded to that gradient. Approximately 5,300 cubic meters of water crosses the transect each year. The flux of water at each location was multiplied by the

average concentration at each location, then summed. The amount of MTBE that moved from the source area across the transect was 2.76 kg/year.

The lower limit on the total quantity of MTBE in the source area was 46 kg. If this flux did not change over time, it would take at least seventeen years to remove the MTBE from the source. If the rate of transfer of MTBE to ground water is proportional to the amount of MTBE in the source, the instantaneous rate of transfer would be 0.06 per year. The average concentration of MTBE at the most contaminated locations within the transect was 1,200 µg/liter. At this rate of attenuation of the source, it would require approximately sixty years for the concentration to reach 30 µg/liter.

Rate of Attenuation of MTBE along Flow Paths

The permanent monitoring wells at the site were sampled for MTBE and BTEX. The rate of attenuation of MTBE at field scale was calculated from the concentration of MTBE in those monitoring wells that were down gradient of the "hot-spot" location CPT-1 (Figure 4). The water was sampled in October 1998. The average hydraulic conductivity was 0.025 cm/sec and the hydraulic gradient was 0.00157. With an effective porosity of 0.25, the calculated seepage velocity was 50 meters per year. Table 2 lists the apparent attenuation of MTBE to the travel time from the source.

TABLE 2. ATTENUATION OF MTBE IN GROUND WITH TIME OF TRAVEL FROM THE SOURCE.

Monitoring Well	Distance from CPT-1 (feet)	Distance from CPT-1 (meters)	MTBE (µg/liter)	Travel Time (years)
CPT-1	0	0	1740	0.0
ESM-14	330	101	383	2.0
ESM-3	450	137	9.73	2.8
ESM-10	590	180	3.9	3.6
ESM-11	790	241	2	4.9

The apparent first-order rate of attenuation of MTBE at field scale was estimated by a linear regression of the natural logarithm of the concentration of MTBE against time of travel from the source. The rate of attenuation of MTBE was 1.54 +/- 1.02 per year at 95% confidence, where the confidence interval reflects variation in spatial distribution of MTBE, and does not reflect uncertainty in the estimate of the seepage velocity.

4. CASE 3: NAVAL CONSTRUCTION BATTALION CENTER, PORT HUENEME, CALIFORNIA

The records of the U.S. Navy Construction Battalion Center (CBC), Port Hueneme, California indicate that approximately 11,000 gallons (42,000 liters) of leaded and unleaded petroleum products were released from underground storage tank lines of a gasoline station between September 1984 and March 1985. Most of the dissolved BTEX compound plumes have been delineated using conventional site characterization methods.

The measured benzene portion of the plume extended no further than 1080 feet (330 meters) down-gradient of the source, while MTBE at a concentration of 16000 µg/liter was identified in a well located approximated 1500 feet or 457 meters from the source. Analysis of samples from ground water monitoring wells in 1997-1998 indicated that the MTBE plume had traveled over 4000 feet (1200 m) of the aquifer from the source. The plume was at least 400 feet (120 m) wide. About 75% of the surface area occupied by the soluble plume only contained MTBE. The BTEX compounds of the spilled gasoline have been attenuated within the remaining residual phase nearer the source (Figure 5).

The site is mostly covered with asphalt, buildings, and concrete pads. Below the surface, there was a layer of fine-grained silty sand to a depth of 7 feet (2.1 m). Below this low permeable layer, began the upper aquifer consisting of a sand and gravel sequence that extended to the clay layer located at 25 feet (7.5 m) below ground surface. The water table ranged from 8.5 to 12 feet (2.6 to 3.7 m) below ground surface. Hydraulic conductivity ranged from 0.3 to 1.4×10^{-3} m/second. The ground water flow was in the direction of southwest at a Darcy velocity 80 to 120 feet (24 to 36 m) per year. With an assumed porosity of 0.3, this corresponds to a seepage velocity of 270 to 400 feet per year.

Core Sampling the Source Area

In July 1999, the Geoprobe™ direct push system was used to acquire core samples in continuous vertical profiles at seven locations in or near the source area (locations at CBC-10, CBC-15, CBC-19, and near air-sparging site). The water table was 9.0 to 10.0 feet below land surface (2.7 to 3.0 meters below land surface) at the time of sampling. The cores extended from the surface to a depth of 15 feet (4.5 m). The cores at each sampling location extended from clean soil above the release, through the release to clean aquifer material below the release. The greatest quantity of aromatic hydrocarbon compounds and MTBE was found at locations near the point of the original leak, near monitoring wells CBC-10 and CBC-19. These two locations also had the greatest mass of MTBE, and the highest concentration of MTBE in the residual fuel at the depth of 10 feet (3 m) where the water table located. At CBC-10, the highest concentration of TPH was 6,000 mg/kg, and the highest concentration of MTBE was 20 mg/kg. At CBC-19, the highest concentration of TPH was 1,100 mg/kg, and the highest concentration of MTBE was 30 mg/kg. The total quantity of fuel hydrocarbons remaining in the source was 4.41 kg/square meter at CBC-10 and 6.89 kg/square meter at CBC-19. The total amount of MTBE remaining was 0.0069 kg/square meter at CBC-10 and 0.023 kg/square meter at CBC-19.

Geochemical Context of the MTBE Plume

The MTBE plume and BTEX plume were contained within a region of the aquifer that was depleted of molecular oxygen. Many regions of the aquifer have less than 0.1mg/liter oxygen. The background concentration of dissolved oxygen was near 0.2 mg/liter. Most regions within the plume area had less than 0.1 mg/liter nitrate. Sulfate concentrations were reduced from a background of near 8000 mg/liter to less than 0.5 mg/liter at the highly contaminated location. The pH of the plume was about 7.2 in the ground water. The oxidation-reduction potentials were measured in the range of -110 mV to -200 mV, which indicated strong reductive conditions in the contaminated aquifer.

Methane concentrations did not exceed 0.3 mg/liter, except one sample acquired from the most contaminated depth on Jun-1998 had a concentration of 3.5 mg/liter. Alkalinity was increased from the background level 375 mg/L CaCO₃ to 1150 mg/L CaCO₃ at the most contaminated location. This showed that as much as 800 mg/liter of alkalinity was produced by oxidation of petroleum hydrocarbons, which corresponded to 350 mg/liter of carbon dioxide produced or 110 mg/liter of TPH consumed. That was more than enough carbon dioxide production to account for the depletion of oxygen and sulfate, and production of Iron II.

Attenuation of MTBE along Plume Path

The permanent monitoring wells at the site along the center of the MTBE plume for two sampling occasions (June 1998 and June 1999) are depicted in Figure 6. MTBE concentrations show a significant declination between two sampling periods (Table 3). The MTBE attenuation rates were calculated from the MTBE concentrations in those monitoring wells down-gradient from the source, CBC-10. The reported average ground water flow velocity was about 30 meters per year. An overall rate of natural attenuation was calculated by a linear regression of the natural logarithm of the concentration of MTBE on travel time down gradient of the sources. The rate of attenuation of MTBE was 0.76 per year for the 1998 data and 0.38 per year for the 1999 data set. At this point the results of the laboratory microcosm study are not conclusive. It is not possible to attribute attenuation to natural biodegradation. The attenuation seen at field scale may be due entirely physical processes such as dilution and dispersion.

TABLE 3. ATTENUATION OF MTBE IN GROUND WATER FROM MONITORING WELLS WITH TIME OF TRAVEL FROM THE SOURCE

Sample	Distance from CBC-10 (feet)	Distance from CBC-10 (meters)	MTBE (µg/L), Jun-1998	MTBE (µg/L), Jun-1999	Travel Time (year)
CBC-10	0	0	38000	4000	0
CBC-15-CS	350	105	5400	1200	0.58
CBC-42	1300	390	4800	770	2.2
CBC-45--CD	2300	690	4600	700	3.8
CBC-49-CS	3400	1020	870	950	5.7
CBC-51	3800	1140	150	320	6.3

5. SUMMARY AND CONCLUSIONS

We have examined case studies of MTBE contamination in ground water at three sites. Each site has own characteristics and geochemical condition, and was taken to represent an important class of MTBE plumes. In the first case study, dissolved oxygen was the dominant electron acceptor, while the second and third cases examined sites where iron reduction and methanogenesis were the major biodegradation processes of BTEX and MTBE.

The extensive monitoring network at the Long Island site allowed the determination of the mass and spatial moments of the contaminant distribution. Total mass of BTEX compound decreased over the three sample rounds, indicating a net loss in the aquifer. MTBE data do not show a clear trend. Because the release or releases which occurred at the Long Island site occurred at unknown times and intervals, much about the contamination at the site remains unknown. By studying the data from the geochemical analysis, the major electron acceptor used for hydrocarbon degradation was found to be dissolved oxygen in ground water. The unique characteristic at the site was the fact that the MTBE plume was distributed behind a "shadow" of older spills of BTEX compounds, where dissolved oxygen was depleted in the ground water. Comparing the MTBE plume and dissolved oxygen distribution revealed that the MTBE plume was restricted to regions in the aquifer that were devoid of oxygen.

The US Coast Guard site showed strong methanogenic and iron reduction conditions. Under these anaerobic conditions, there was evidence of the attenuation of MTBE in the distribution of the MTBE plume and in a mass balance analysis. A rate of attenuation rate could be estimated from the field data.

The US Navy site was under sulfate reducing and iron reducing conditions. It was only methanogenic in the area in contact with residual LNAP. The rate of natural attenuation was much less than that from the US Coast Guard site, where methanogenic conditions pertained throughout the plume.

After several years of study and field work at a variety of sites under different geochemical conditions, we have collected evidence that natural attenuation of MTBE in ground water is important in some plumes, but not in others. Even though the attenuation of MTBE is not fast, it can be estimated and quantified at field scale. Several research projects are ongoing to provide a better understanding of the natural attenuation processes of MTBE in ground water.

DISCLAIMER

The study in this document has been funded wholly or in part by the United States Environmental Protection Agency, the United States Coast Guard, the United States Navy, and New York State Department of Environmental Protection. It has not been subjected to Agencies' review. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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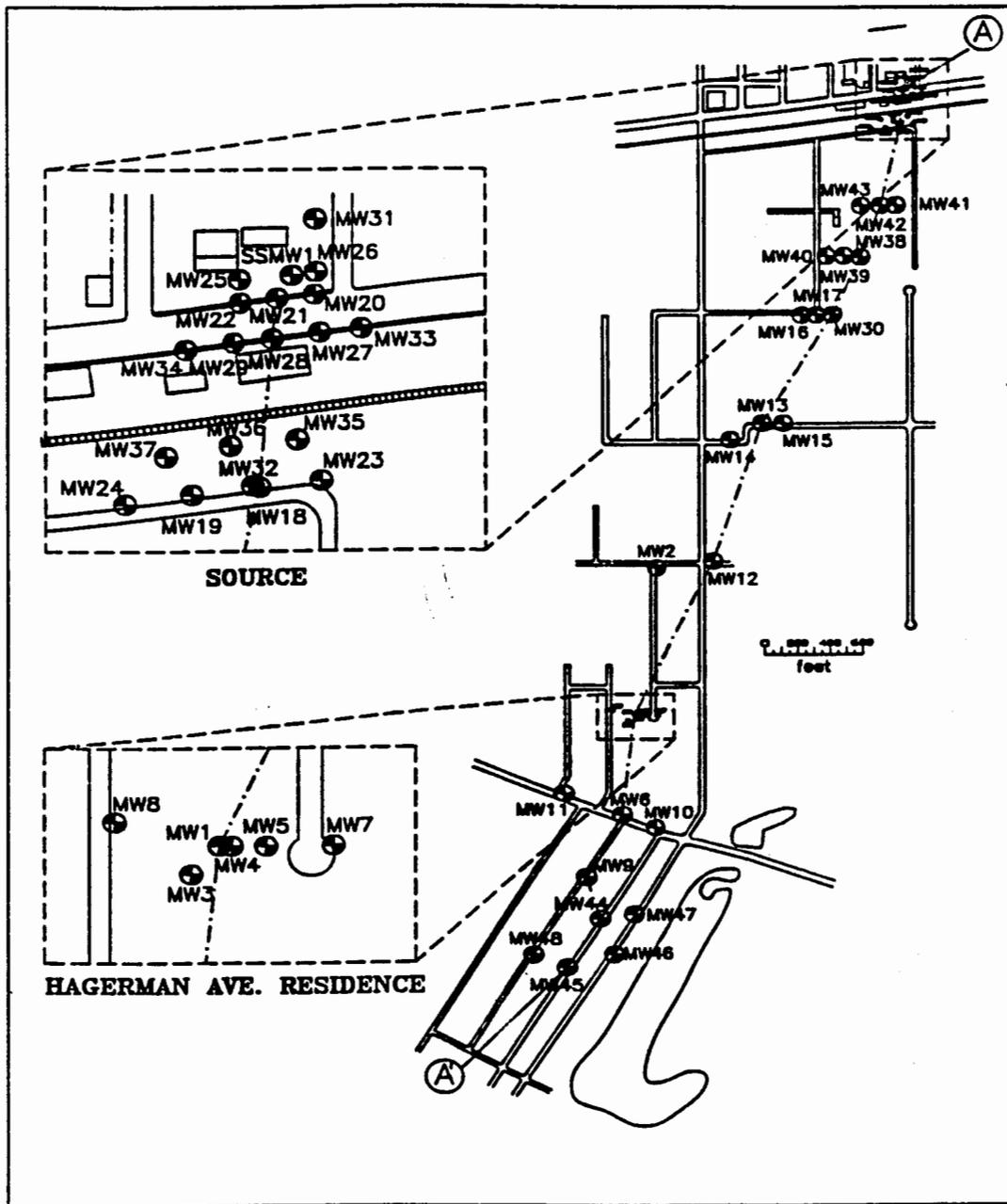


Figure 1. Service Station Site, Long Island, NY

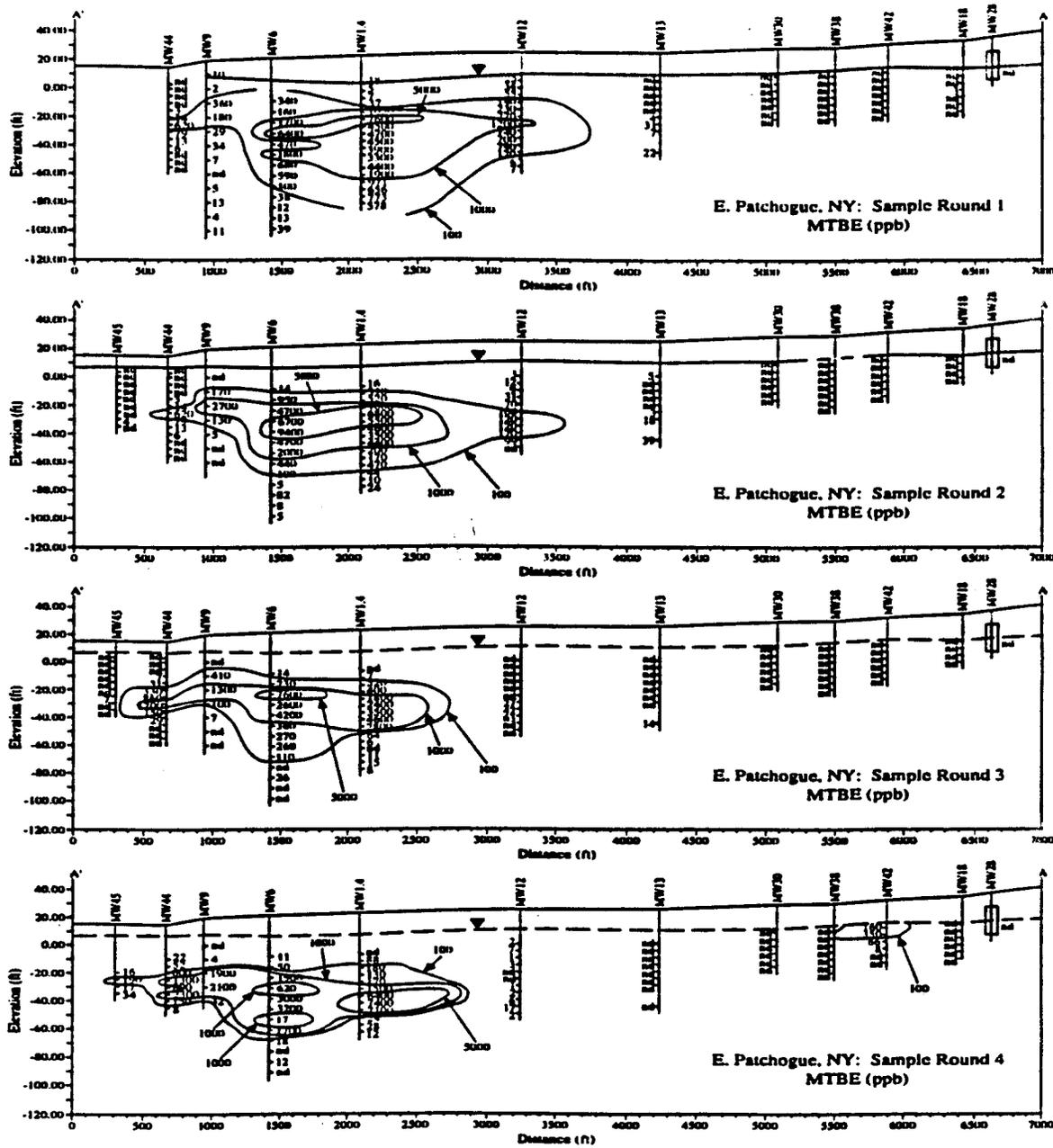


Figure 2. MTBE Distribution in Ground Water, Long Island, NY

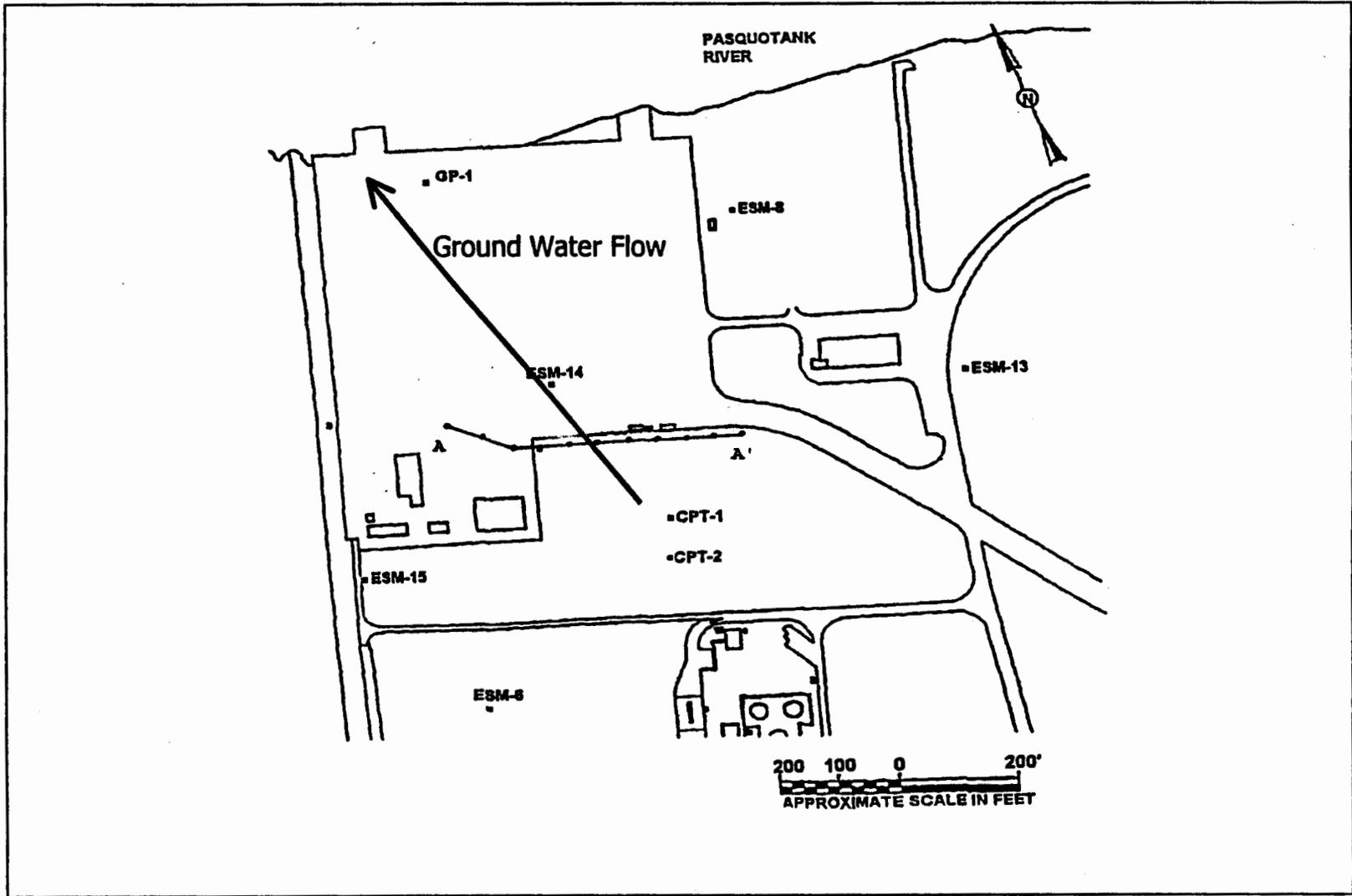


Figure 4. Fuel Tank Farm Site, US Coast Guard Supply Center, Elizabeth City

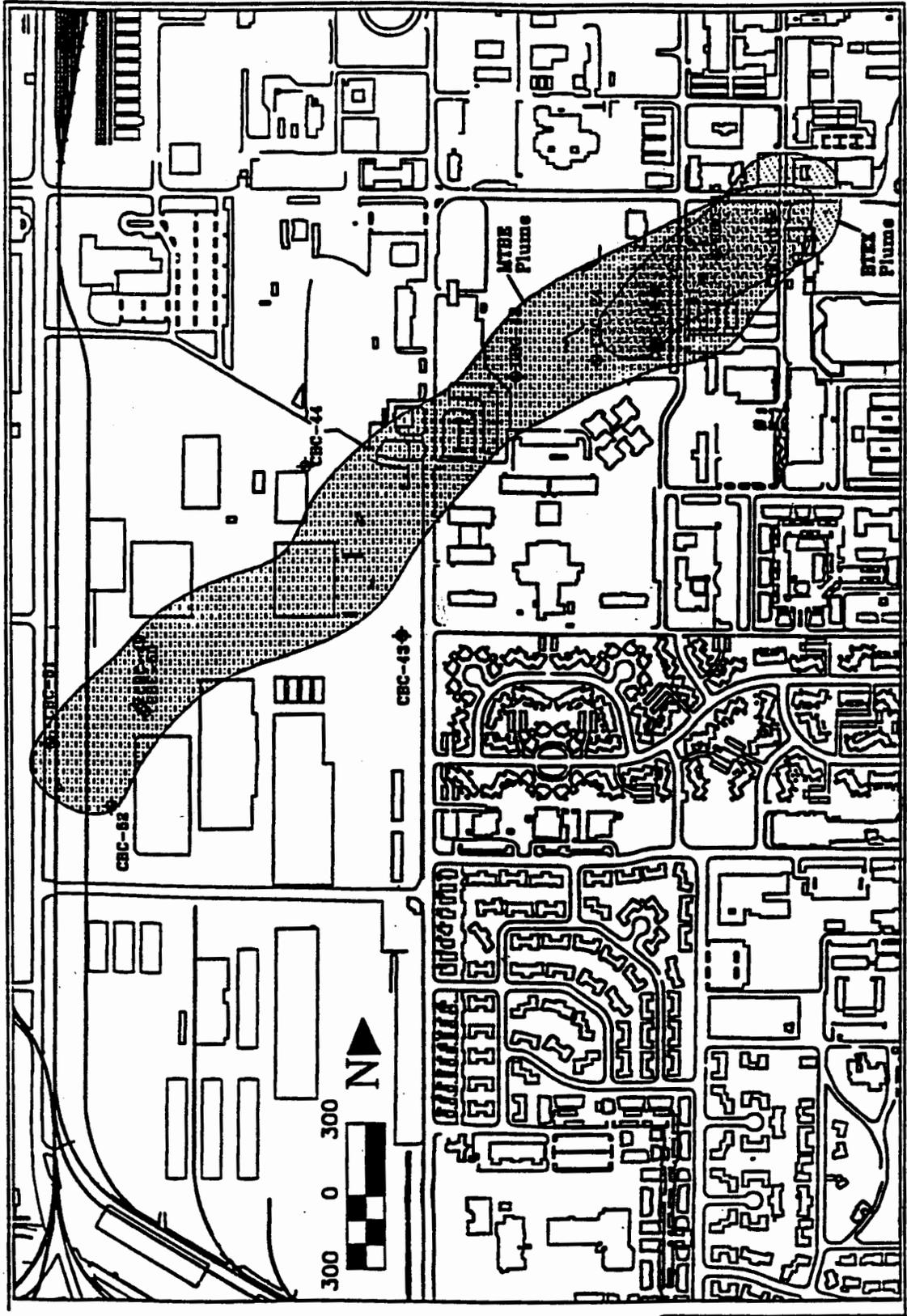


Figure 5. BTEX and MTBE Plume, US Navy, Port Hueneme, CA

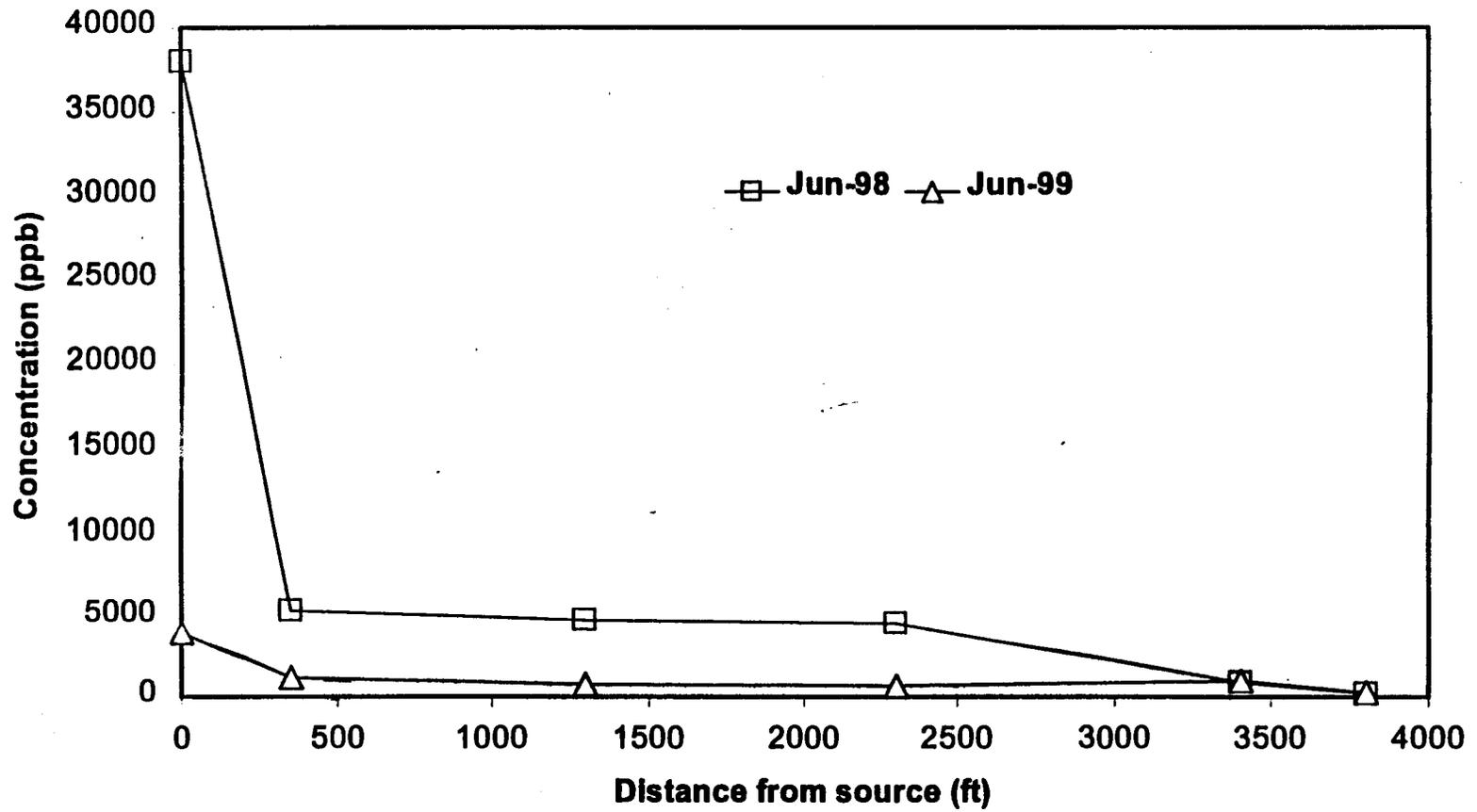


Figure 6. MTBE Concentration Changes along Plume Center, US Navy

TECHNICAL REPORT DATA		
NRMRL-ADA-00114		
1. REPORT NO. EPA/600/A-02/010	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE NATURAL ATTENUATION OF MTBE	5. REPORT DATE	
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16. ABSTRACT Three cases of MTBE contamination of ground water are presented. Each case site had own characteristics and different geochemical condition. The first case site was where dissolved oxygen was the dominant electron acceptor, while the sites of the second and third cases were under the anaerobic conditions where iron reduction and methanogenesis were the major biodegradation process of BTEX and MTBE. At the first case site, total mass of BTEX compounds decreased over the three sampling rounds, indicating a net loss in the aquifer. MTBE data did not show a clear trend. Under then anaerobic conditions of the second and third cases, the attenuation of MTBE could be evidenced from the MTBE plume distribution data and mass balance analysis. Through several years of study and field works at several sites under different geochemical conditions, we could collect evidence of the natural attenuation of MTBE in ground water. Even though the attenuation was not fast compared to those of BTEX compounds, it was noticeable and the rate could be estimated.		
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