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## Analysis of the Gasoline Spill at East Patchogue, New York

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### Abstract

Gasoline containing methyl *tert*-butyl ether (MTBE) was released from a service station in East Patchogue, Long Island, New York. The resulting plume of contaminated ground water was over 1800 m (6000 feet) long, and resulted in the closing of private water supply wells. Data from a three-dimensional monitoring network were used to estimate the mass and position of the center of mass of benzene, toluene, ethylbenzene, xylenes and MTBE contaminant plumes. The monitoring network was sampled on three occasions so temporal information on the evolution of the plume was available. By estimating the moments of the contaminant distributions for each of the sample rounds, the loss of mass of each contaminant was estimated, as was the rate of migration of the center of mass. An estimate of the volume of gasoline released was made from plausible estimates of the gasoline composition.

### Introduction

Over 300,000 releases from leaking underground storage tanks have been reported to state regulatory authorities (USEPA, 1995). Depending on a number of factors, chemicals which compose fuels may form contaminant plumes in the ground water. Field and laboratory investigations have established that the most important of these (benzene, toluene, ethyl benzene and the xylenes [BTEX]) are degradable under most conditions (see e.g., Rifai et al., 1995). Oxygenated additives that are

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used as octane enhancers and as mandated by the Clean Air Act have also found their way into subsurface water supplies (Squillace et al., 1995). The purpose of this paper is to describe a gasoline release that occurred in East Patchogue, New York and to use chemical data collected from the aquifer to estimate the mass and location of center of mass of each constituent, the gasoline release volume, and the ground water flow velocity. A companion paper describes simulation modeling of the site (Weaver, 1996b).

## Background

Published studies of groundwater flow on Long Island indicate that a regional ground water divide lies along the length of the island and to the north of the geographic centerline (Eckhardt and Stackelberg, 1995). South of the divide, flow is generally toward the Atlantic Ocean. Buxton and Modica (1993) estimate that the hydraulic conductivity of the upper glacial aquifer is on the order of  $8.1 \times 10^{-2}$  cm/sec (230 ft/day) in the outwash section near the southern shore, with estimated ground water velocities of  $3.5 \times 10^{-4}$  cm/sec (1 ft/day) or greater.

Table 1 lists the density,  $\rho$ , solubility,  $S$ , organic carbon partition coefficient  $K_{oc}$ , fuel/water partition coefficient,  $K_o$ , and the mass fraction in gasoline,  $x$ , of MTBE and the BTEX compounds.  $K_{oc}$  values were taken from Mercer and Cohen, (1990) and US EPA (1990). The fuel/water partition coefficient and mass fraction data were measured by Cline et al. (1991) on 31 samples of gasoline from Florida. The range reported covers the variation in measured mass fractions in samples from other parts of the continent and from lists of typical gasoline compositions (see e.g., Cline et al., 1991, Corapcioglu and Baehr, 1987).

The usage of methyl *tert*-butyl ether, MTBE, began on Long Island in the late 1970s, after EPA approved its usage as an octane enhancer. Initial usage of MTBE on Long Island was likely in the range of 5% by volume. Oxygenated additives were mandated to reduce carbon monoxide emissions in 39 cities, including New York City and Long Island, by the 1990 amendments to the Clean Air Act. State of New York regulations have required use of fuel with oxygen content between 2.7% and 2.9% in the winter months since 1992 (State of New York, 1995). The most commonly used oxygenated additive is MTBE, which provides the required oxygen content at about 15% MTBE by volume.

The subsurface behavior of MTBE is notable for two reasons. First, MTBE is highly water soluble. As a measure of the solubility, the fuel/water partition coefficient for MTBE is about 23 times lower than that for benzene and 280 times lower than those for m- or p-xylene (Table 1). The release of MTBE from gasoline, therefore, is expected to be much more rapid than the release of BTEX.

The second notable fact about MTBE is its recalcitrance to biodegradation. Microcosm studies conducted with three soils showed no degradation of MTBE over a 250 day study period under anaerobic conditions (Yeh and Novak, 1994). Degradation

Chemical	density g/mL	solubility mg/L	$K_{oc}^{(a)}$ L/kg	$K_o^{(b)}$	$x^{(c)}$ % (mass)
MTBE	0.74	48000	11.2	15.5	–
benzene	0.88	1750	83 (65)	350	1.73 (0.7-3.8)
toluene	0.87	535	300 (257)	1250	9.51 (4.5-21.0)
ethyl benzene	0.87	152	1100 (676)	4500	1.61 (0.7-2.8)
m-xylene	0.86	130	982 (691)	4350	<sup>(d)</sup>
p-xylene	0.86	196	870 (691)	4350	<sup>(d)</sup>
o-xylene	0.88	175	830 (691)	3630	2.33 (1.1-3.7)

<sup>(a)</sup> Organic carbon partition coefficient reported by Mercer and Cohen (1990), the second value (in parenthesis) from US EPA (1990).

<sup>(b)</sup> Fuel/water partition coefficient reported by Cline et al. (1991).

<sup>(c)</sup> Mass fraction of chemical in gasoline reported by Cline et al. (1991).

<sup>(d)</sup> m- and p-xylene were not differentiated they composed 5.95% with range of 3.7% to 14.5%.

Table 1: Chemical parameter values

tion was induced under anaerobic conditions with the addition of nutrients, a hydrogen source and molybdate in an organic-poor soil. In organic rich soils degradation of MTBE could not be induced. Horan and Brown (1995) concluded MTBE degradation might occur at a very low rate, however, under aerobic conditions. In a controlled field study, gasoline with 10% MTBE, and an 85% methanol/15% gasoline blend were released in the same aquifer (Hubbard et al., 1994). MTBE was found to be recalcitrant to degradation, while methanol and BTEX were degraded. Further, the MTBE had no measurable effect on the degradation of the other compounds.

### Site History

Subsurface contamination was detected at E. Patchogue, New York when water from a residential well on Hagerman Avenue became undrinkable. The site investigation began at the well and expanded through the drilling of monitoring wells in the up-gradient and down-gradient directions (Figure 1). The purpose of the drilling was to delineate the extent of contamination and locate the suspected source. Ultimately, the source was traced back to an abandoned service station approximately 1200 m (4000 ft) up-gradient from the Hagerman Avenue residence. Soil borings in the area of the service station confirmed the presence of hydrocarbon contamination. The service station's tanks are believed to have been removed in 1988, which is the latest date that gasoline could have been released. In 1994 and 1995, the contaminant plume was mapped from samples taken from 26 multilevel samplers and

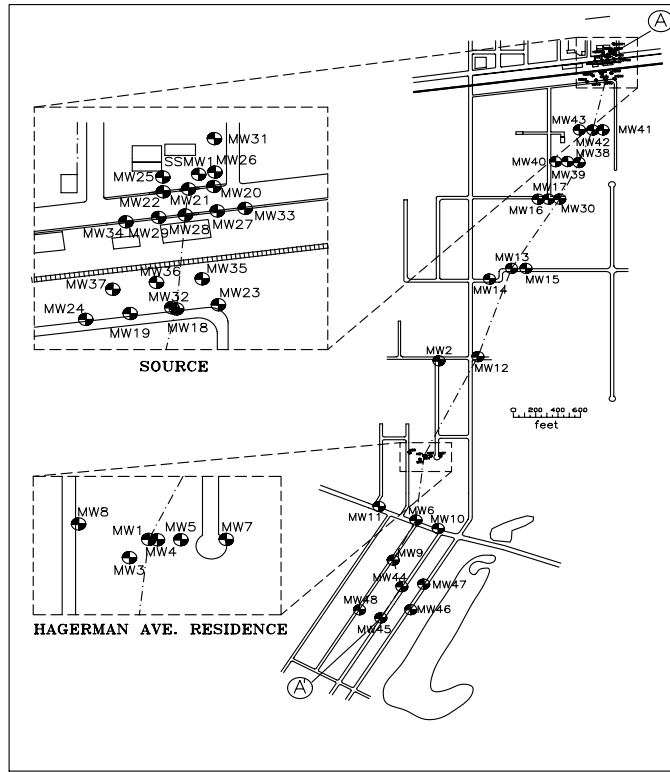


Figure 1: Hagerman Avenue Site Plan.

22 monitoring wells. Water samples from three sample rounds were analyzed for BTEX and MTBE. Total organic carbon contents were determined on 11 clean core samples.

### Moments Analysis

The relatively large number of monitoring wells and multilevel samplers generated a three-dimensional data set, which were analyzed by calculating the moments of each concentration distribution. The moments,  $M^{ijk}$ , are defined by

$$M^{ijk} = \iiint x^i y^j z^k n C(x, y, z) dx dy dz \quad (1)$$

where  $x$ ,  $y$ , and  $z$  are the moment arms,  $n$  is the porosity,  $C(x,y,z)$  is the concentration. These moments can be used to estimate the mass of the contaminant distribution, given by the zeroth moment,  $M^{000}$ . Likewise the first moments can be used to determine the center of mass of the distribution:

$$x_c = \frac{M^{100}}{M^{000}} \quad y_c = \frac{M^{010}}{M^{000}} \quad z_c = \frac{M^{001}}{M^{000}} \quad (2)$$

where  $x_c$ ,  $y_c$ , and  $z_c$  are the  $x$ ,  $y$ , and  $z$  coordinates of the center of mass of the distribution.

The challenge in applying equation 1 to field data is in evaluating the integrals. The SITE-3D program developed by US EPA for visualization of site data (Weaver, 1996a) was used to generate the moment estimates by dividing the contaminant plume into a set of nearest-neighbor polygons. The polygons represent zones of influence of each well. In essence, the polygons replace the explicit interpolation schemes between sampling locations that have been used in other analyses (Freyberg, 1986 among others).

For most of the plume, the wells cross the entire width of the plume. In some locations, however, monitor wells with high contaminant concentrations are located on the edge of the sampling network (MW-12, MW-30, MW-38, MW-39). Therefore some of the contaminant mass is not included in the estimates given below. Because the MTBE is located down-gradient of MW-30, MW-38, and MW-39, its mass estimates were not greatly impacted.

## Results

Table 2 shows the mass estimates and the distance of the center of mass of the contaminant distribution from the contaminant source,  $d_{com}$ . The data in sample round one were taken as the wells were installed from July 1994 to March 1995. The average date of the first sample round, weighted by number of samples taken, is December 16, 1994. Data from sample round two were taken from April 11, 1995 to April 20, 1995 and those from sample round three were taken from October 10, 1995 to October 24, 1995. Since the samples in round one were taken over a long time period, contaminants sampled up-gradient may have been transported to down-gradient receptor wells before they were sampled. The order of sampling, however, proceeded up-gradient from the discovery point (MW-1) to the suspected source, followed by the wells down-gradient from MW-1.

Each of the chemicals listed in Table 2 has some tendency for sorption. Since the chemical data come from water samples, the sorbed mass must be estimated. Chemicals sorb in proportion to the fraction of organic carbon in the aquifer material,  $f_{oc}$ , and the chemical's organic carbon partition coefficient,  $K_{oc}$ . Sorption was assumed to follow the linear equilibrium isotherm as given by

$$C_{xs} = K_{oc} f_{oc} C_{xw} \quad (3)$$

where  $C_{xs}$  is the sorbed concentration of contaminant  $x$  expressed per unit mass of aquifer solids, and  $C_{xw}$  is dissolved concentration of chemical  $x$ . The sorbed mass of contaminants was estimated from

$$M_{xs} = \frac{\rho_b}{n} K_{oc} f_{oc} M_{xw} \quad (4)$$

Chemical	Sample Round One			Sample Round Two			Sample Round Three		
	$M_{xw}^{(a)}$	$M_{xs}^{(b)}$	$d_{com}^{(c)}$	$M_{xw}$	$M_{xs}$	$d_{com}$	$M_{xw}$	$M_{xs}$	$d_{com}$
	kg	kg	m	kg	kg	m	kg	kg	m
MTBE	268	24	1387	386	34	1557	229	20	1583
B	241	156 (122)	991	117	76 (59)	1004	58	38 (29)	1061
T	108	253 (217)	230	65	152 (130)	298	60	141 (120)	306
E	29	249 (153)	347	24	206 (127)	347	21	180 (111)	326
X	149	1041 (804)	222	95	663 (513)	277	92	643 (497)	272

- (*a*)  $M_{xw}$  is the mass dissolved in ground water.
- (*b*)  $M_{xs}$  is the mass sorbed to the aquifer solids, estimated from the  $K_{oc}$  reported by Mercer and Cohen (1990) and, in parenthesis, from that reported by US EPA (1990).
- (*c*)  $d_{com}$  is the distance from the suspect source to the center of mass of the contaminant distribution.

Table 2: Moment based estimates of mass and center of mass

where  $M_{xs}$  and  $M_{xw}$  are the respective sorbed and dissolved masses of chemical  $x$ , and  $\rho_b$  is the bulk density. Organic carbon contents were determined for 11 uncontaminated samples taken from 4.88 m to 8.23 m (16 ft to 27 ft) below the ground surface near the source region. The arithmetic average of  $f_{oc}$  was 0.126%, with range of 0.009% to 0.627% and standard deviation of 0.190%. The porosity and solids density were assumed to equal 0.30 and 2.65 g/cm<sup>3</sup>, respectively, giving a bulk density of 1.86 g/cm<sup>3</sup>. The  $K_{oc}$  values were taken from Table 1. Table 2 lists estimated sorbed masses for each chemical.

The estimated mass of benzene, toluene, ethyl-benzene and the xylenes decreased between each sample round. Each of these compounds is expected to undergo biodegradation in the aquifer, but each continued to dissolve into the aquifer through from October 1995. The latter fact is 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. The distribution of MTBE was such that in all sample rounds, no MTBE was found between the source and a point approximately 600 m (2000 ft) down-gradient (Figure 2). Thus it appears that the MTBE was almost entirely leached from the gasoline near the source.

The average concentrations over the entire plume are given in Table 3. These concentrations were calculated from the pore volume estimates and measured concentrations at all points in the sampling network where concentrations were above the detection limit.

### Estimation of the Mass of Gasoline Released

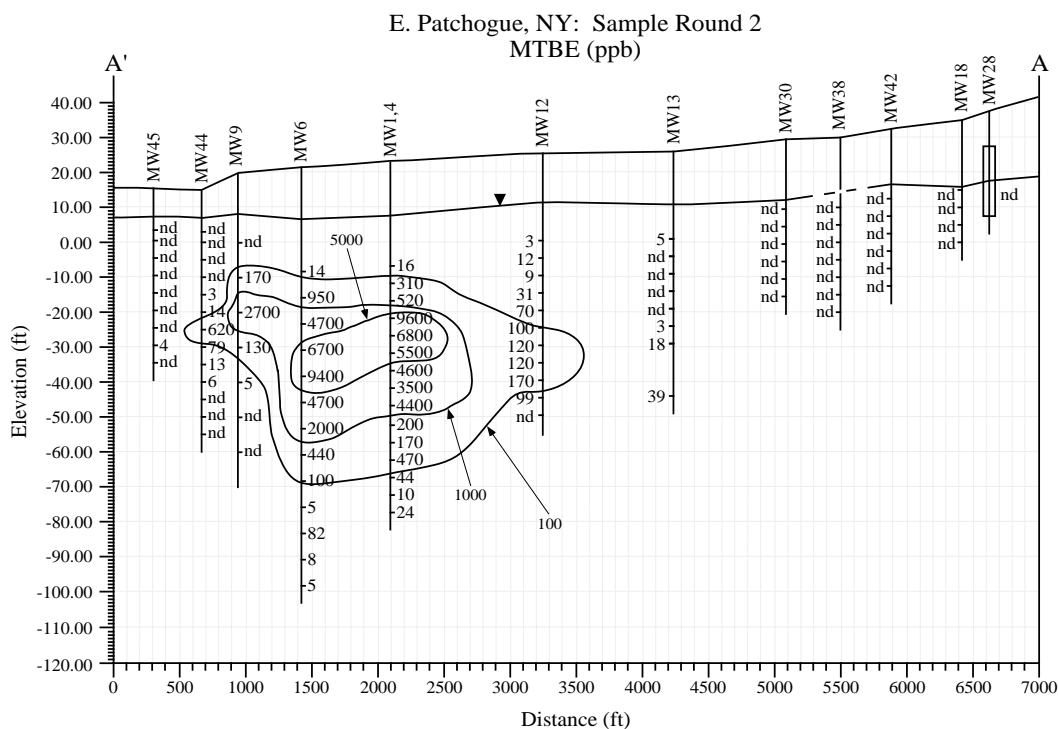


Figure 2: Distribution of MTBE in sample round two

The mass of contaminants in the aquifer can be used to place bounds on the volume of gasoline released. The estimated mass of MTBE in the aquifer is 292 kg for sample round one and 420 kg for sample round two. Since the gasoline must have been released before the Clean Air Act mandates, MTBE was assumed to comprise 5% by volume of the gasoline. The corresponding volume of gasoline for these estimated masses would be 7.89 m<sup>3</sup> (2080 gallons) and 11.35 m<sup>3</sup> (2999 gallons). Because of the apparent complete leaching of MTBE from the gasoline, this estimate would represent the entire volume of MTBE enhanced gasoline released to the aquifer.

The BTEX data suggest the volumes of gasoline listed in Table 4, assuming that the density of the gasoline was 0.72 g/cm<sup>3</sup>. In the absence of specific knowledge concerning the composition of the released gasoline, the estimates developed by Cline et al., (1991) (see Table 1) were used in estimating the gasoline volumes in Table 4. Unlike MTBE each of the BTEX chemicals persists in gasoline at the source (Figure 3). More of the benzene originally contained in the gasoline, however, would be in the aquifer than any of the other BTEX compounds because of benzene's lower fuel/water partition coefficient. A greater fraction of each of T, E and X remain in the gasoline because of their higher affinities for the gasoline phase (expressed in Table 1 by their lower water solubilities and higher fuel/water partition coefficients).



Chemical		Sample Round One mass kg	Gasoline Volume Estimates (gal)		
			mass fraction from Cline et al., 1991		
			low	middle	high
benzene	( <i>a</i> )	397	20807	8567	3832
	( <i>b</i> )	363	19025	7834	3505
toluene	( <i>a</i> )	361	2943	1393	631
	( <i>b</i> )	325	2650	1255	568
ethyl benzene	( <i>a</i> )	278	14624	6335	3643
	( <i>b</i> )	182	9539	4148	2385
xylenes	( <i>a</i> )	1190	9096	5273	2399
	( <i>b</i> )	953	7284	4223	1921

(*a*) Mass estimate using  $K_{oc}$  of Mercer and Cohen (1990)

(*b*) Mass estimate using  $K_{oc}$  of USEPA (1990)

Table 4: Gasoline volume estimates from BTEX mass estimates

water velocity and can be estimated from the position of the center of mass of the distributions during each sample round. These moment-based estimates include concentration changes, presumably caused by transport, from all sample locations, and thus average fast and slow moving portions of the plume. Generally, in sample round one the data were collected from the down-gradient wells first, followed by those nearer the source. Thus 101 days passed between the average sample date for sample round one and sample round two. The wells near the Hagerman Avenue residence, however, were sampled 216 days before the sampling for sample round two. Sample rounds two and three were separated by 186 days. Based upon these durations, average rates of advance of the contaminant plumes are given in Table 5.

Because of the long duration of sample round one, the most reliable of the results are those for sample round two to three. The aquifer properties and gradients are presumed to vary with space, so the velocities may depend on position. For example, the gradient is lower at the down-gradient end of the plume, which may have caused the MTBE plume to move slower between sample rounds two and three than did the benzene plume, because the center of mass benzene plume was approximately 500 m up gradient from the MTBE center of mass (Table 2). The increase in average MTBE concentration from sample rounds one to three supports this contention as mass could be accumulating down-gradient, causing the average concentration to increase (Table 3). Also, as shown in Figures 2 and 3, the vertical thickness of the plume increases down-gradient. The velocity of the center of mass should decrease in the thicker part of the plume by mass balance, because the mass of contaminants fills a larger volume. The average MTBE concentration would be expected to decrease, which it does not (Table 3), however. The centers of mass of both the ethyl benzene and xylenes plumes retreated from sample round two to sample round three. This suggests that the rate of input of mass of these compounds to the aquifer is less

than the rate of their loss.

Chemical	Rate of Advance (m/d)		
	Sample Rounds		
	One to Two 101 d	Two to Three 216 d	Two to Three 186 d
MTBE	1.68	0.79	0.14
benzene	0.13	0.06	0.30
toluene	0.67	0.31	0.04
ethyl benzene	0	0	-0.11
xylenes	0.56	0.27	-0.02

Table 5: Average rate of advance of the contaminant plumes

### Conclusions

The extensive monitoring network at the Hagerman Ave site allows determination of the mass and moments of the contaminant distributions. The accuracy of the mass estimates depends upon the sampling network, duration of sample events, and the accuracy of the procedure used for forming the estimates. Each of these introduces uncertainty into the estimates presented in this paper.

The mass of each of the BTEX compounds appears to decrease over the three sample rounds, indicating a net loss of mass in the aquifer. MTBE data do not show a clear trend. The mass of each contaminant in the aquifer can be used to give an estimate of the volume of the gasoline release. The mass of MTBE in the aquifer represents approximately 11.35 m<sup>3</sup> (2999 gallons) of MTBE-enhanced gasoline. Since MTBE was not used regularly before 1992, this gasoline volume estimate is likely to be low. From sample round one, the mass of benzene gives a maximum lower bound estimate of approximately 50 m<sup>3</sup> (13200 gallons), if the benzene composed 1 % by mass of the gasoline. Since the released gasoline composition is unknown, this estimate can be considered a tentative estimate of the gasoline volume. The masses of the other BTEX compounds gave lower gasoline volume estimates which are thereby consistent with the estimate from the benzene. The rates of advance of the contaminant plumes can give estimates of the ground water velocity. From sample rounds two and three, MTBE advanced 0.14 m/d (0.5 ft/d) which gives a plausible velocity for the down-gradient portion of the site.

The mass of the release influences all activities at a contaminated site. Because the release or releases which occurred at Hagerman Avenue occurred at unknown times and intervals, much about the contamination at the site remains unknown. By studying the data from the gasoline release, estimates of important quantities have been developed. Although, the values are not completely certain, they represent

plausible estimates for the site.

### Disclaimer

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