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Use of Long-Term Monitoring Data to Evaluate Benzene, MTBE, and TBA Plume Behavior in Groundwater at Retail Gasoline Sites

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Abstract: Long-term groundwater monitoring data for 48 retail gasoline sites were analyzed to define the characteristics of affected groundwater plumes containing benzene, methyl tert-butyl ether (MTBE), and tert-butyl alcohol (TBA). Results of this analysis were used to determine the observed range and statistical distribution of current plume lengths, plume stability conditions, constituent concentration trends and attenuation rates, and the remediation timeframe for this population of sites. The goal of this evaluation was to characterize plume behavior as observed across a variety of hydrogeologic settings, on the basis of detailed groundwater monitoring records, rather than to define the site-specific factors controlling plume behavior. The results indicate that MTBE plumes in groundwater underlying a majority of these underground storage tank sites that were monitored for five years or longer (1) have significantly diminished in concentration over time, (2) are comparable in length to benzene plumes, (3) are, like benzene plumes, principally stable or shrinking in size and concentration, and (4) are on track to achieve remedial goals within a timeframe comparable to or faster than that of benzene plumes. At these same sites, TBA plumes were found to be comparable to benzene and MTBE plumes in terms of plume length. However, whereas most TBA plumes are also stable or shrinking, the percentage of TBA plumes that are currently stable or shrinking (68%) is less than that for benzene plumes (95%) or MTBE plumes (90%), likely reflecting the temporary build-up of TBA concentrations in groundwater attributable to methyl tert-butyl ether (MTBE) biodegradation. Nevertheless, overall trends for TBA concentrations in groundwater indicate that TBA is attenuating at rates comparable to benzene and MTBE and can be expected to meet applicable remediation goals in a similar timeframe as the other gasoline constituents. **DOI: 10.1061/(ASCE)EE.1943-7870.0000488.** © *2012 American Society of Civil Engineers.*

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Introduction

In the 1990s, detections of methyl tert-butyl ether (MTBE) in the groundwater at petroleum storage tank sites and water supply wells generated considerable scientific and regulatory concern regarding the potential effect of this relatively new gasoline fuel additive on groundwater resources [USGS 1995; California Environmental Protection Agency (CEPA) 1999; USGS 2001]. In contrast to non-oxygenated gasoline fuel constituents, MTBE was known to be highly soluble in water, with low sorption coefficients, and was understood to be relatively recalcitrant to natural biological activity (Yeh and Novak 1991; Suflita and Mormile 1993; Hubbard et al. 1994; Mormile et al. 1994; Neilson 1994). As a result, some scientists predicted that, in comparison with non-MTBE gasoline, releases of MTBE-containing gasoline from underground storage tank (UST) sites would result in relatively long plumes of affected groundwater that would cause much longer-term effects on groundwater resources and drinking water supplies (Fogg et al. 1998; Odencrantz 1998; Weaver and Small 2002). These predictions were supported by the discovery of a few exceptionally long MTBE plumes extending thousands of feet down-gradient of the release point, such as in Long Island, New York (Weaver et al. 1996; Weaver et al. 1999).

However, studies evaluating actual field measurements of hundreds of MTBE plumes across the United States and abroad have found the true extent and duration of MTBE effects on groundwater to be much less than previously anticipated. Specifically, monitoring data for groundwater plumes at nearly 400 gasoline release sites in California (Happel et al. 1998; Shih et al. 2004), Texas (Mace and Choi 1998; Shorr and Rifai 2002; Rifai et al. 2003), South Carolina (Wilson et al. 2003), and Florida (Reid et al. 1999; Reisinger et al. 2000) show that MTBE plumes typically stabilize at relatively short lengths (< 200 ft), which are comparable to those of benzene plumes. Additionally, groundwater monitoring results from a total of 81 sites evaluated in Texas in 2002 (Shorr and Rifai 2002) and in Florida in 1999 (Reid et al. 1999) indicate that the majority of MTBE plumes (75%) are stable or decreasing in length. Furthermore, with regard to MTBE concentrations in individual monitoring wells, data from a total of 1628 monitoring wells in Texas (Rifai et al. 2003) and Connecticut (Stevens et al. 2006) indicate that MTBE concentrations in the groundwater are stable or decreasing over time in 74% of the wells evaluated. Research outside of the United States similarly reported the effects of MTBE

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on potable groundwater sources to be relatively limited on a regional scale. For example, in England and Wales, modeling analyses based on 3,000 groundwater samples from over 800 sites found that the potential plume dimensions for ether oxygenates, such as MTBE, did not pose a major threat to public water supplies (Environment Agency 2000). Additionally, a review of groundwater conditions at a number of sites with exceptionally large MTBE plumes discovered in the 1990s (Fogg et al. 1998; Odencrantz 1998; Weaver and Small 2002) indicate that the MTBE plume length and concentrations have diminished significantly over time [Environmental Assessment & Remediations (EAR) 2005; EAR 2011; New York State Department of Environmental Conservation (NYSDEC) 2011].

Nevertheless, some of these studies indicate that their conclusions may be of limited applicability or certainty owing to the short duration of groundwater monitoring history analyzed for individual sites (< 1 to 3 years) and/or insufficient evaluation of the plume stability condition (Happel et al. 1998; Shih et al. 2004). Employing short-term data to predict long-term plume trends can entail uncertainty because (1) short-term groundwater monitoring data are more vulnerable to seasonal fluctuations and sampling variability; and (2) employing short-term monitoring records could underestimate the true rate of attenuation of compounds, such as MTBE, that require longer acclimation periods to undergo biodegradation. Similarly, characterization of the plume stability condition is important for understanding whether the current plume length represents the maximum area of effect or if further plume expansion could occur.

In addition, recent reports on complex groundwater plumes (e.g., detached and/or diving plumes), such as those located in the Long Island, New York area (Weaver and Wilson 2000; Nichols and Roth 2006), in California (Wilson et al. 2004), in Illinois (Wilson et al. 2005), and in dual-porosity aquifers such as the Cretaceous Chalk in the United Kingdom (Thornton et al. 2006), note the importance of adequate monitoring networks to achieve detailed horizontal and vertical delineation of groundwater plumes at typical UST sites. In the absence of adequate horizontal and vertical delineation, failure to identify detached plumes or diving plume conditions could result in misinterpretation of the groundwater conditions at UST sites, such as underestimation of actual plume lengths. This study evaluates hydrogeologic conditions at each site to identify those sites at which diving plumes may be of concern because of elevated recharge rates, vertical flow gradients, and/or absence of stratigraphic features serving to impede downward plume migration.

The present study attempts to improve the understanding of MTBE plume behavior by (1) evaluating a database of geographically diverse sites with long-term groundwater monitoring records and (2) employing a comprehensive analytical approach that includes evaluation of current plume stability (including the potential for detached and diving plume conditions), current plume length, temporal concentration trends in groundwater, and attenuation rates for MTBE at these sites. In addition to MTBE, the behavior of benzene and tert-butyl alcohol (TBA) plumes in groundwater are evaluated and the long-term behavior of these three constituents in groundwater at these sites are compared. Benzene is used in this study as a representative component of non-MTBE fuel, for which the fate and transport characteristics in groundwater were well defined in prior studies, such as Weidemeier et al. 1999. TBA, an intermediate biodegradation product of MTBE, was shown to biodegrade in both aerobic and anaerobic environments (Zeeb and Weidemeier 2007). Evaluation of these three chemicals in groundwater at petroleum release sites is intended to characterize the behavior of MTBE relative to that of benzene, and the MTBE degradation product, TBA.

Methodology

This study was conducted using monitoring records from a database of 48 retail gasoline sites with historical detections of benzene and MTBE in groundwater. For this purpose, long-term monitoring records for UST sites, corresponding to sites with complete records for at least six monitoring wells for five years or more, were solicited from regulatory agencies, energy companies, and environmental consultants. Of an initial population of 54 sites, the number of sites found to meet the screening criteria was 48 for benzene, 48 for MTBE, and 38 for TBA. At each site meeting the minimum data requirements, plume behavior for each constituent was characterized by evaluating the current length, the current stability condition, the temporal concentration trends, the observed attenuation rates, and the timeframe necessary to achieve applicable remediation goals.

The groundwater remediation goals used to define the length of the affected groundwater plumes and evaluate the timeframe to achieve remediation endpoints are as follows: 5 μg/L for benzene, 10 μg/L for MTBE, and 12 μg/L for TBA. For benzene, the remediation goal corresponds to the federal maximum contaminant level (MCL) for drinking water (5 μg/L), (EPA 2009). For MTBE, the value corresponds to the New York State Department of Environmental Conservation (NYSDEC) groundwater standard for MTBE (10 μg/L), (NYSDEC 2008) and for TBA, the value corresponds to the California drinking water action goal (12 μg/L) (RWQCB 2004). The reported laboratory detection limits for groundwater analyses at the 48 sites evaluated in this study were rarely above the concentration limits (benzene = 6%; MTBE = 9%; TBA = 14%), providing an appropriate level of sensitivity to evaluate current compliance with remediation goals.

The following section describes the site database used in this study and the methodology used to evaluate plume behavior at each site.

Database of Long-Term Groundwater Monitoring Records for UST Sites

Key characteristics of the groundwater monitoring database for the 48 sites included in this study are as follows:

- Geographic location: The sites are located in various states in the United States with different histories of MTBE use; specifically, 63% of the sites are in California, 19% in New Jersey 10% in Alaska, 6% in Oregon, and 2% in Nevada. A majority of the sites (82%) are located in California and New Jersey, two states that together, represented 45% of the total MTBE consumption in the United States in 2001 (Lidderdale 2003).
- Current site use: Of the 48 UST sites, 30 are active service stations and 18 are inactive stations or vacant lots with no further potential for releases of gasoline.
- Release history: Available information indicates that underground fuel storage tanks and dispenser islands were principal sources of release of leaded and/or unleaded gasoline at the 48 sites evaluated. More than 70% of the 48 sites have records of releases occurring after 1992 or are active service stations that handled MTBE reformulated gasoline (RFG) after 1992.
- Environmental effects: Non-aqueous phase liquid (NAPL) or sheen was reported in monitoring wells at 34 of the 48 sites. Groundwater impacts were reported to be limited to a shallow aquifer unit at a majority of the sites, with only 6% of the sites reporting effects to more than one aquifer zone.

- Groundwater monitoring program: For the 48 sites included in this study, the median number of groundwater monitoring wells per site is 17, with a median of four wells located in the source area ("source wells"), seven wells located within the plume downgradient of the source ("plume wells"), and six wells located outside of the affected groundwater plume ("delineation wells"). In this study, only wells designated as either source wells or plume wells were used to evaluate plume concentration trends. The median length of time that groundwater monitoring was underway at the 48 sites is 15 years for benzene, 11 years for MTBE, and eight years for TBA. Additionally, for the purpose of calculation of point attenuation rates, only those wells with more than eight years of monitoring data were used.
- Remediation history: For 44 of the 48 sites evaluated in this study, information was available regarding past or on going remedial actions for affected groundwater. In sum, seven sites (16%) were managed only by monitored natural attenuation (MNA); nine sites (20%) were addressed only with NAPL recovery; 13 sites (30%) received some form of active groundwater remediation (e.g., pump and treat, air sparging) without NAPL recovery; and 15 sites (34%) received some form of active groundwater remediation in combination with NAPL recovery.

As indicated by the relatively extensive monitoring well networks, the long groundwater monitoring periods, the past presence of NAPL, and the implementation of active remedies at a majority of the sites in this study, this database is more representative of sites with larger fuel releases and more extensive groundwater impacts as opposed to sites with only minor MTBE effects on groundwater (e.g., with a few monitoring wells showing low-μg/L concentrations of MTBE in groundwater). Consequently, the findings of this study should be understood to pertain to plumes at sites with relatively significant fuel releases and not to sites with de minimis releases of MTBE at which much shorter plume lengths and durations may be observed.

Evaluation of Groundwater Plume Behavior

For each of the 48 sites in this study, the behavior of the affected groundwater plume was evaluated as follows:

1. Plume stability: The current plume stability condition was characterized by two methods: (1) comparing the maximum spatial extent of the groundwater plume observed historically with the spatial extent observed during the most recent sampling event at the site and (2) evaluating long-term concentration trends in the wells located at the downgradient edge of the plume using the Mann-Kendall statistical method, as described in the MAROS software system [Air Force Center for Environmental Excellence (AFCEE) 2000]. For each constituent, the plumes were then classified as shrinking, stable, expanding, no trend, or detached. Plume concentration trends were characterized using the Mann-Kendall statistical method, as described in Aziz et al. (2003), as follows: (1) an increasing trend refers to a Mann-Kendall result of increasing with a significance level $> 90\%$; (2) a decreasing trend refers to a Mann-Kendall result of decreasing with a significance level $> 90\%$; (3) a stable condition refers to a Mann Kendall result of no trend at a significance level $> 90\%$ and with a coefficient of variation (COV) < 1 (indicating low degree of variability); and (4) no trend refers to a Mann-Kendall result of no trend but with a significance level $< 90\%$ and a high degree of variability ($COV > 1$). Using this approach, plume stability was evaluated for benzene at 42 sites, for MTBE at 41 sites, and for TBA at 34 sites.
2. Current measured and estimated plume length: Current plume lengths were determined either by (1) measuring the distance from the source location to the downgradient location meeting the remediation goal (i.e., a clean location), for those sites in which the existing monitoring well network included at least one clean downgradient well (designated as well-delineated plumes in this study); or (2) estimating the distance from the source to a clean downgradient location, using an empirical estimation method on the basis of the observed bulk attenuation rate (Newell et al. 2002), for those sites at which the current monitoring well network did not include a clean downgradient well. Plumes for which the lengths could not be either directly measured or estimated were designated as indeterminate.

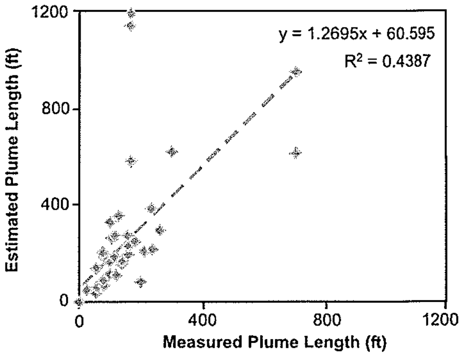

Fig. 1. Correlation between estimated ersus measured plume lengths at 30 UST sites with well-delineated MTBE, benzene, and TBA plumes

The available data were sufficient to provide measurements of plume length for 26 benzene plumes, 28 MTBE plumes, and 19 TBA plumes. These well-delineated plumes were considered the more reliable measure of plume length and were consequently used to check the plume length estimation method used for plumes with less complete delineation. As shown in Fig. 1, the estimated plume lengths for the well-delineated plumes, derived using the bulk attenuation rate, show a reasonable correlation to the true measured plume lengths at these sites (slope = 1.2, $R^2 = 0.43$), with the error tending toward overestimation of the true plume length in most cases. On this basis, this calculation method was considered a conservative method for estimating the plume length for those sites with less complete delineation. Using this methodology, estimated plume lengths were derived for an additional eight sites for benzene, seven sites for MTBE, and three sites for TBA.

Indeterminate plume lengths were found at 19% of the benzene sites, 15% of the MTBE sites, and 35% of the TBA sites in this study. To account for the effect of these indeterminate lengths on the plume population statistics (specifically, the median plume length), as a highly conservative measure the indeterminate plumes were assumed to be equal to or longer than the longest measured or estimated plume length determined for each constituent.

Additionally, to ensure that the available monitoring data provided a reliable measure of true plume dimensions, at each site and for each constituent the possible occurrence of a diving plume was evaluated on the basis of available data for vertical delineation of the plume. This entailed review of groundwater test results from the deeper monitoring wells on each site to confirm that the plume did not extend downward beyond the depth of the monitoring network, resulting in possible mischaracterization of the true plume length. Furthermore, each site was evaluated using the EPA plume dive calculator (Weaver and Wilson 2000) to determine whether site-specific hydrogeologic conditions could result in downward displacement of the plume sufficient to extend beyond the depth of the monitoring well network. Results of this analysis found none of the sites to pose a concern with regard to diving plumes. Stratigraphic features at each site may have played an important role in limiting plume dive in the groundwater underlying these sites (Wilson et al. 2005).

3. Current plume concentration trends: To evaluate the long-term temporal trends of constituent concentrations in groundwater at the 48 sites, monitoring data from individual wells that was sampled during eight or more sampling events, with detectable concentrations reported in four or more of these sampling events, were evaluated as follows:

   (1) Concentration trends in individual wells: To assess the trend of concentration versus time within each well, monitoring data from individual wells were statistically evaluated using the Mann-Kendall method, as described in the MAROS software system (AFCEE 2000). Additionally, to minimize the effect of analytical variability and data censoring attributable to the detection limit, only wells in which individual constituents had historically been detected above 20 $\mu g/L$ were evaluated for concentration trends. Of the 589 source wells and plume wells installed at the 48 sites, 288 wells (43 sites), 306 wells (42 sites), and 241 wells (34 sites) met these minimum criteria for benzene, MTBE, and TBA, respectively.

   (2) Current versus historical compliance with applicable remediation goals: Monitoring data from individual wells that were sampled during at least one event after 2007 were evaluated for past and current compliance with the applicable remediation goals. In total, 218 wells (33 sites), 279 wells (34 sites), and 134 wells (22 sites) met these selection criteria for benzene, MTBE, and TBA, respectively.

   (3) Changes in maximum groundwater concentrations at individual sites over time: Additionally, as a simple measure of the change in plume concentrations over time on a site-wide basis, the maximum historical concentration of each gasoline constituent detected in any well during the initial 20% of the monitoring history at a site was compared with the maximum concentration reported at any well during the most recent sampling event conducted at the site after 2007. At the 48 sites, maximum concentrations of gasoline constituents measured in groundwater ranged between 45 $\mu g/L$ and 120,000 $\mu g/L$ for benzene, between 23 $\mu g/L$ and 1,700,000 $\mu g/L$ for MTBE, and between 68 $\mu g/L$ and 700,000 $\mu g/L$ for TBA. Reduction in maximum groundwater concentrations over time were evaluated at 42 sites for benzene, 41 sites for MTBE, and 34 sites for TBA.

4. Point attenuation rates in individual wells and at sites: A first-order rate of attenuation of chemical concentrations in the groundwater aquifer was calculated for each source well and plume well that exhibited a stable or decreasing concentration trend by estimating the slope of the lognormal plot of concentration versus time [lnC versus t; point attenuation rate, as defined in Newell et al. (2002)] for benzene, MTBE, and TBA at each well.

5. Additional and total remediation timeframe: For the purpose of this study, the additional remediation timeframe corresponds to the estimated future period required from the date of the last monitoring episode for each site (typically 2009) until the maximum constituent concentration measured at the site is reduced to the applicable remediation goal. This additional timeframe for each site was calculated using the site-specific average point attenuation rates (see point 4 above) and the most recent maximum concentration for each constituent (Newell et al. 2002). The total remediation timeframe for each compound was calculated as the sum of (1) the duration of groundwater monitoring period following the first detection of the constituent at the site and (2) the maximum estimated additional remediation timeframe necessary to meet the applicable remediation goal for that constituent. Using this approach, additional and total remediation timeframes were evaluated at 37 sites for benzene, 31 sites for MTBE, and 15 sites for TBA.

MTBE-degrading microbes are understood to require longer acclimation periods than the microbes that degrade benzene, toluene, ethylbenzene, and xylene (BTEX) constituents (Shah et al. 2009). Consequently, to avoid underestimating the true rate of biodegradation of MTBE in the groundwater, this evaluation included only those wells with long-term monitoring records (> 8 years) with detectable concentrations of gasoline constituents measured above the detection limit during four or more sampling events. Additionally, to ensure that the observed changes in the concentration were attributable to attenuation rather than an artifact of variable laboratory results or detection limits between sampling events, only those wells that exhibited concentrations above 200 $\mu g/L$ for each gasoline constituent during the initial 20% of its monitoring history were used to calculate the point attenuation rate for that constituent. Using this approach, point attenuation rates were calculated for 187 wells (38 sites), 165 wells (30 sites), and 62 wells (16 sites) for benzene, MTBE, and TBA, respectively.

The "total remediation timeframe" for each compound was calculated as the sum of (1) the duration of groundwater monitoring period following the first detection of the constituent at the site and (2) the maximum estimated additional remediation timeframe necessary to meet the applicable remediation goal for that constituent. Using this approach, additional and total remediation timeframes were evaluated at 37 sites for benzene, 31 sites for MTBE, and 15 sites for TBA.

Results of Data Evaluation

Plume Stability

The results show that the vast majority of the benzene plumes (95%) and the MTBE plumes (90%) evaluated in this study are stable or diminishing in size (see Fig. 2). Less than 5% of benzene

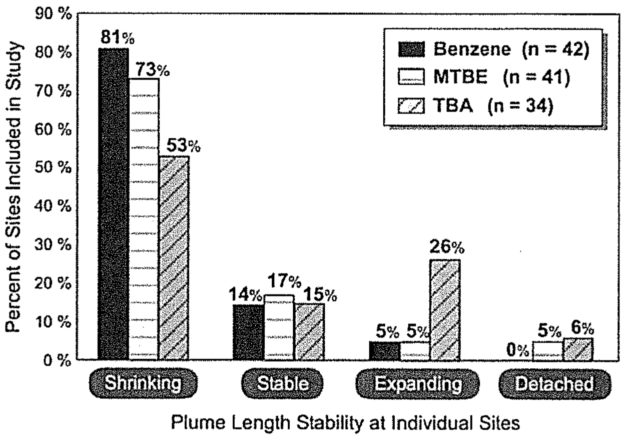

Fig. 2. Results of groundwater plume stability evaluation at individual sites

plumes (2 of 42 sites) and MTBE plumes (2 of 41 sites) were observed to be expanding in size over time. MTBE plumes showed evidence of being detached from the original release area at a small number of sites (2 of 41 sites); however, comparison of the past and current dimensions of these detached MTBE plumes shows that the spatial extent of on-site and off-site groundwater impacts for these detached plumes is also diminishing in size. None of the 42 benzene plumes exhibited detached conditions.

For TBA, 68% of the plumes evaluated (23 of 34 sites) are currently stable or shrinking in size, whereas 26% (9 of 34 sites) were observed to be expanding in size over time. At the remaining two sites (6%), TBA was detected at higher concentrations in the plume wells than in the source wells, indicating a detached plume condition. The higher percentage of expanding TBA plumes (26%) compared with that of its parent compound MTBE (approx. 5%) suggests that, at some sites, biodegradation of MTBE has contributed to increased concentrations of TBA in the areas downgradient of the plume source area.

In summary, in terms of plume stability, MTBE plumes closely match the behavior of benzene plumes, with the vast majority of the MTBE plumes investigated (> 90%) being in a stable or diminishing condition. Additionally, preliminary evaluation of the MTBE footprint at the few sites with detached plumes shows that on-site and off-site groundwater impacts are now much smaller in size than in the past, thus suggesting that, similar to normal groundwater plumes, detached plumes also stabilize and attenuate over time and distance. Although a majority of the observed TBA plumes are also stable or diminishing (68%), the lower percentage relative to MTBE and benzene plumes likely reflects the temporary build-up of TBA concentrations in groundwater attributable to MTBE biodegradation. In general, TBA may persist within the portion of the plume where biodegradation of benzene, MTBE, and other gasoline constituents has depleted available electron acceptors, and then preferentially biodegrade in the downgradient portions of the plume, where higher concentrations of suitable electron acceptors are encountered.

Current Measured and Estimated Plume Lengths

For the purpose of this evaluation, plumes lengths were (1) measured directly for well-delineated plumes, (2) estimated using a conservative empirical relationship, or (3) characterized as indeterminate on the basis of available data (see the discussion in the Methodology section above). Results of the plume length evaluation for each category of plume are provided below and in Fig. 3.

1. Measured plume lengths for well-delineated plumes: For sites with well-delineated plumes, the current median plume lengths, as measured by the monitoring well network, are 105 feet for benzene (26 sites), 75 feet for MTBE (28 sites), and 118 feet for TBA (19 sites) [see Fig. 3(a)]. The 90th percentile plume lengths for benzene, MTBE, and TBA at these same sites were 208 ft, 210 ft, and 226 ft, respectively. As a population, no statistically significant difference existed between MTBE plume lengths and benzene plume lengths at the same sites, as determined using the Student's t-test ($p = 0.69$). The two MTBE plumes found to be detached from the source area exhibited plume lengths of 550 ft (with a maximum downgradient extent 700 ft from the original source zone) and 510 ft (with a maximum downgradient extent 885 ft from the original source zone).
2. Estimated plume lengths: For sites with stable or shrinking plumes at which the existing well network was not adequate to delineate the plume length but for which a bulk attenuation rate could be calculated (on the basis of a lnC versus distance plot), plume lengths were estimated using the method described in Newell et al. (2002) (see the discussion in the Methodology section above). For this population of sites, the current median estimated plume lengths are 354 feet for benzene (eight sites), 379 feet for MTBE (seven sites), and 371 feet for TBA (three sites) [see Fig. 3(b)].
3. Measured and estimated plume lengths: In combination, the current median plume lengths were measured or were estimated to be 125 feet for benzene (34 of 42 sites), 110 feet for MTBE (35 of 41 sites), and 145 feet for TBA (22 of 34 sites) [see Fig. 3(c)]. For this data set, the 90th percentile plume lengths for benzene, MTBE, and TBA are 356 ft, 454 ft, and 366 ft, respectively [see Fig. 3(b)].
4. Measured, estimated and indeterminate plume lengths: The plume length values presented above do not include indeterminate plumes, for which the plume lengths could not be measured or estimated on the basis of available data, corresponding to 19% of the benzene plumes (8 of 42), 15% of

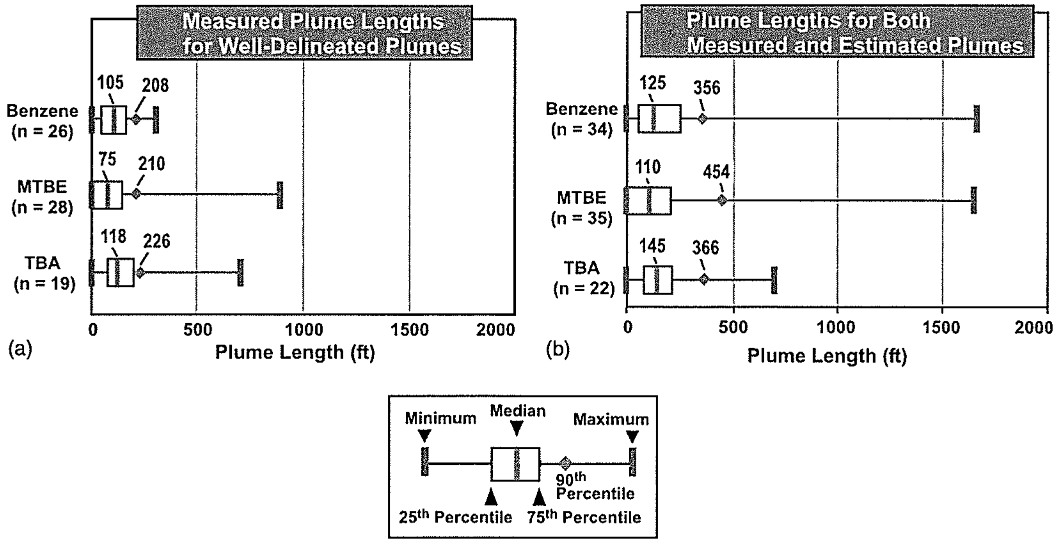

Fig. 3. Distribution of (a) measured plume lengths for well-delineated plumes; (b) measured and estimated plume lengths for all plumes

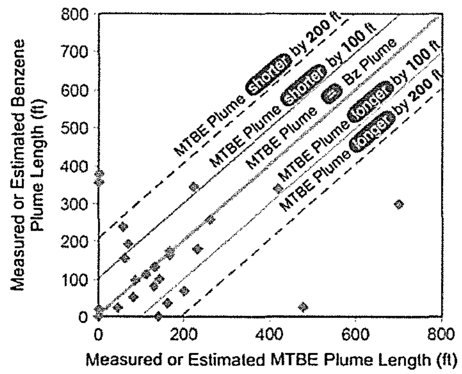

Fig. 4. Comparison of measured or estimated plume lengths for benzene versus MTBE

MTBE plumes (6 of 41), and 35% of TBA plumes (12 of 34) in our data set.

Given that these indeterminate plumes extended beyond the extent of the existing monitoring well networks, expecting that the average length of these plumes would exceed the average length of the plumes whose lengths were delineated or estimated is reasonable. Therefore, as a conservative measure, the median lengths of the full plume population, including the indeterminate plumes, were estimated using highly conservative assumption that all of the indeterminate plumes are equal to or longer than the longest measured or estimated plume length. Given this assumption, the adjusted median plume lengths for the full population of measured, estimated, and indeterminate plumes are 171 feet for benzene, 140 feet for MTBE, and 235 feet for TBA. These values correspond to a very conservative high-end estimate of median plume lengths and may significantly over estimate the true median plume length for this population.

(5) Comparison of MTBE and benzene plume lengths: On a site-by site basis, at the 33 sites at which both MTBE and benzene plumes were measured or estimated, the MTBE and benzene plumes are not statistically different on the basis of a Student's t-test analysis (assuming two-tail distribution and unequal variances between populations; p = 0.23). Fig. 4 provides a comparison of the MTBE and benzene plume lengths determined for these 33 sites. As shown, 70% of the MTBE and benzene plumes (23 of 33) are within +/ − 100 feet in length, whereas only 12% of sites (4 of 33) contained plumes that differed by more than 200 ft (see Fig. 4).

In summary, for the sites in this study, the lengths of MTBE plumes are comparable to those of benzene plumes (adjusted median values of 140 feet for MTBE versus 171 feet for benzene for all plumes, and unadjusted 90 percentile plume lengths of 454 feet for MTBE versus 356 feet for benzene for measured and estimated plumes). TBA plume lengths are also comparable to those of MTBE plumes (adjusted medians of 235 feet for TBA versus 140 feet for MTBE for all plumes, and unadjusted 90 percentile plume lengths of 366 feet for TBA versus 454 feet for MTBE for measured and estimated plumes).

Note that the applicable MTBE remediation goal employed in this study (i.e., 10 μg/L) is more stringent than groundwater standards applied in some states in the United States, including California (primary $MCL = 13$ μg/L) [California Department of Public Health (CDPH) 2009] and New Jersey ($MCL = 70$ μg/L) [New Jersey Department of Environmental Protection (NJDEP) 1997]. Consequently, the plume lengths presented in this paper represent a conservative overestimate of MTBE plume lengths subject to remedial action goals in those states.

Current Groundwater Concentrations and Concentration Trends

(1) Reductions in the maximum plume concentrations observed at each site: The monitoring records show that the maximum plume concentrations recorded within the initial 20% of the monitoring period decreased over time for 93, 90, and 74% of the benzene (40 sites), MTBE (38 sites), and TBA (26 sites) plumes evaluated in this study. Among these sites, the median reductions over time in the maximum historical groundwater concentration were 90%

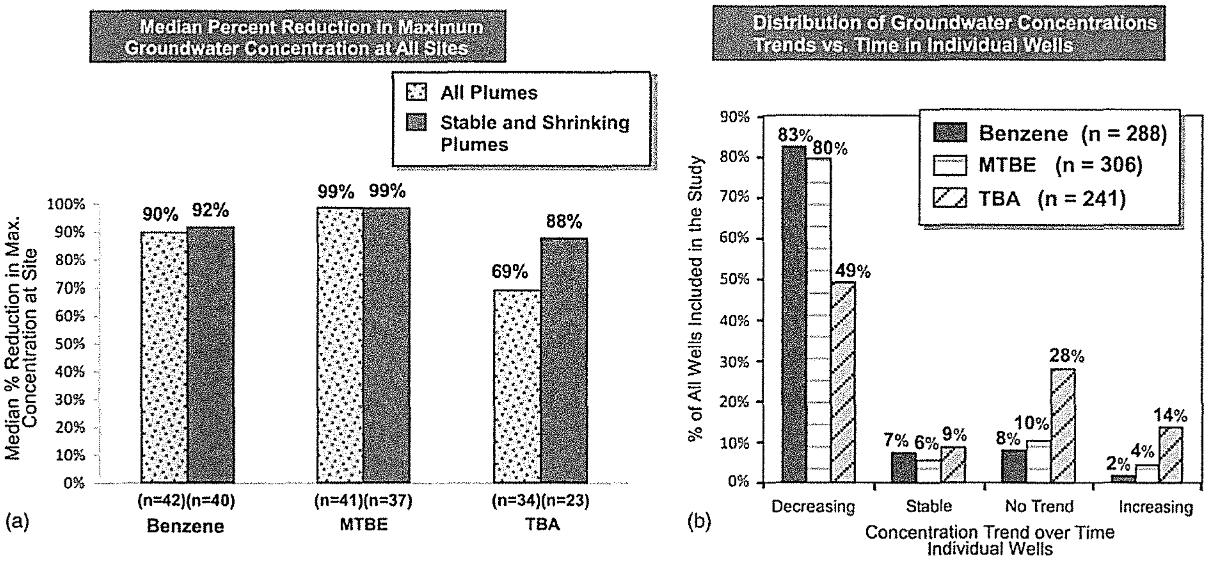

Fig. 5. Concentration Trends: (a) Median percent reduction in maximum groundwater concentration at all sites; (b) distribution of groundwater concentrations trends versus time in individual wells (Both stable plumes and no trend plumes have a Mann-Kendall result of "no trend." However, for our evaluation, consistent with the MAROS guidelines (Aziz et al. 2003), "stable" is used for "no trend" results for which the level of significance is $> 90\%$ and $COV < 1$, whereas no trend refers to no trend results with level of significance $< 90\%$ and/or $COV > 1$)

for benzene, 99% for MTBE, and 69% for TBA [see Fig. 5(a). For those sites with shrinking or stable plumes, the percentage reductions in the maximum historical concentrations were slightly higher than for the full plume population, at 92% for benzene (40 sites), 99% for MTBE (37 sites), and 88% for TBA (23 sites). At sites with detached MTBE plumes (two sites) or TBA plumes (two sites), the concentration reduction was observed to be approximately 92% for MTBE and 81% for TBA.

(2) Concentration Trends in Individual Monitoring Wells: Evaluation of the concentration trends in individual monitoring wells found concentrations to be stable or diminishing over time for 90% of wells with detectable benzene and for 86% of wells with detectable MTBE [see Fig. 5(b)]. Less than 2% of the wells containing benzene and less than 4% of the wells containing MTBE exhibit increasing concentration trends. For TBA, 58% of individual wells show stable or diminishing concentration trends over time, whereas 13% of the wells exhibit increasing trends.

(3) Current versus historical compliance with applicable remediation goals:

All wells: The number of monitoring wells that meet the remediation goals for benzene and MTBE increased significantly over the monitoring periods [see Fig. 7(a)]. Specifically, the percentage of individual monitoring wells that meet the selected remediation goals (i.e., 5 μg/L for benzene and 10 μg/L for MTBE) increased from 10 to 48% for benzene and from 11 to 57% for MTBE, representing an approximate five-fold increase in compliance for each constituent. The percent of individual monitoring wells for which TBA meets the selected remediation goal (12 μg/L) also increased, but by a lesser margin than the other two constituents, increasing to 25% in the most recent sampling episodes compared with 16% historically, an approximate 60% increase. In general, the percentage of plume wells in compliance with the remediation goal is greater than those located in the source area, which is consistent with the commonly observed pattern of concentrations diminishing more rapidly in the downgradient portion of the plume, with measurable concentrations persisting for a longer period in the source area.

Site-wide evaluation: On a site-wide basis (i.e., in 100% of monitoring wells), 12% of the 43 sites affected by benzene, 24% of the 42 sites affected by MTBE, and 14% of the 35 sites affected with TBA presently meet the applicable remediation goal for all monitoring wells [see Fig. 6(b)]. Historically, none of these sites met the remediation goal on a site-wide basis for all monitoring wells.

In summary, during the monitoring period, the majority of sites investigated in this study experienced significant reductions in maximum plume concentrations for benzene, MTBE, and TBA (i.e., > 69% of sites for all three compounds). The median reduction observed in the maximum concentration in MTBE plumes (99%) exceeds that of benzene plumes (90%) for the full plume populations [see Fig. 5(a)]. Within individual monitoring wells, MTBE exhibits concentration trends comparable to those of benzene, with 86 to 90% of wells showing stable or diminishing concentrations over time. As a result, a much larger percentage of wells now comply with these remediation goals than was observed at the beginning of the monitoring period. Relative to benzene and MTBE plumes, a smaller percentage of TBA wells (58%) exhibit stable or diminishing concentrations, whereas a larger percentage indicate increasing concentrations (13%), which may reflect the temporary increase in TBA concentrations attributable to biodegradation of MTBE.

Detached MTBE and TBA plumes exhibit concentration reductions (MTBE: 85 to 99% reduction; TBA: 71 to 91% reduction) similar to those of non-detached plumes (MTBE: 29 to 100% reduction; TBA: 11 to 100% reduction). The median concentration reduction exhibited by all TBA plumes (69%) is less than that of MTBE (99%) and benzene plumes (90%), possibly reflecting the temporary build-up of TBA concentrations attributable to biodegradation of MTBE.

Point Attenuation Rates in Individual Wells

For wells exhibiting a trend of stable or diminishing concentrations over time, the data are amenable to calculation of a point attenuation rate (i.e., on the basis of C versus t) using the standard methods described in Newell et al. (2002). (Note that, in this paper, when concentrations are declining over time, the rate constant has a negative value; when concentrations are increasing over time, the rate constant is positive). The concentration attenuation rates observed in individual wells for the three gasoline constituents under study are as follows.

(1) Point attenuation rates in individual wells: First-order point attenuation rates estimated for benzene in 188 wells (39 sites)

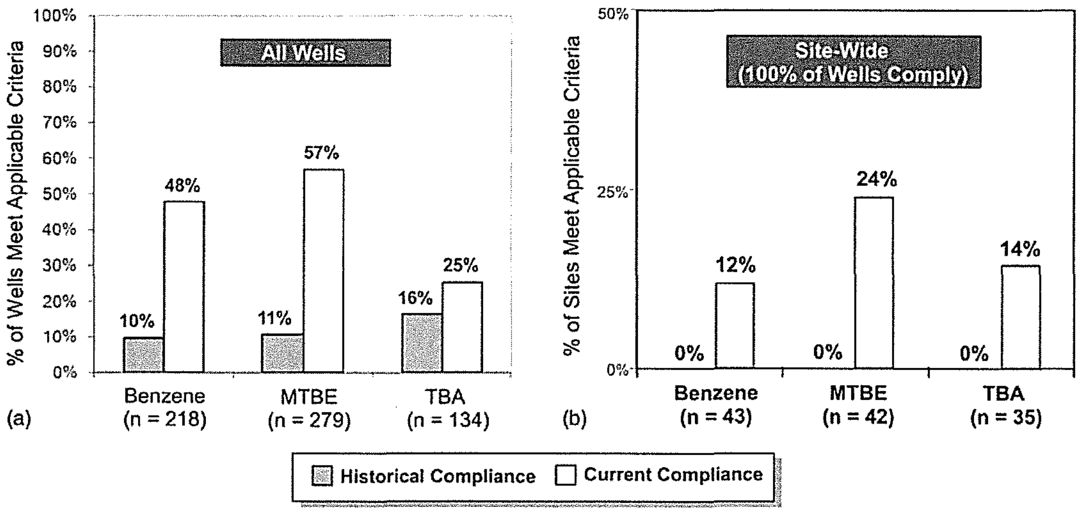

Fig. 6. Comparison of historical versus current compliance with remediation goals

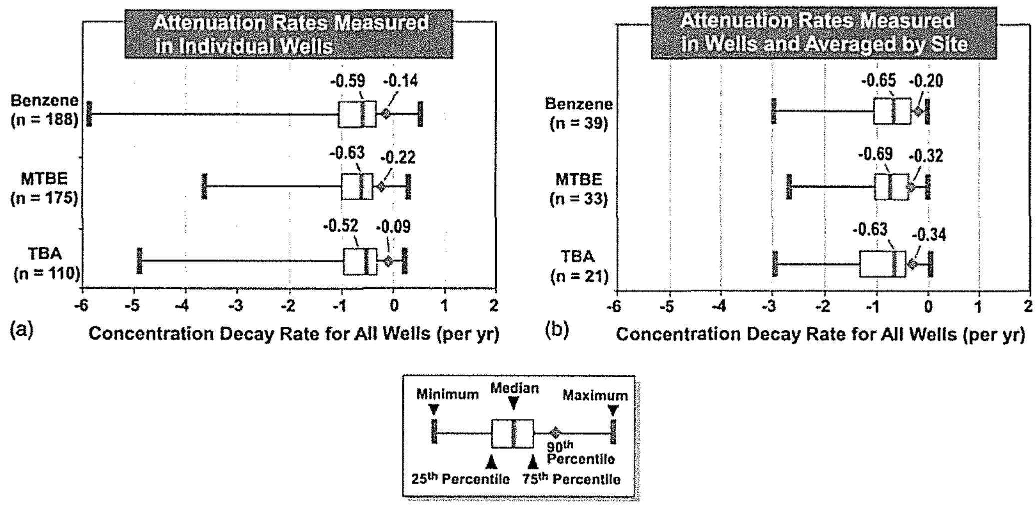

Fig. 7. Comparison of point attenuation rates for benzene, MTBE, and TBA at sites with stable or shrinking plumes

ranged from −5.8 per year to 0.52 per year, with a median value of −0.59 per year [see Fig. 7(a)]. For MTBE, first-order attenuation rates were estimated for 175 wells (33 sites) and were observed to range from −3.6 per year to 0.29 per year, with a median value of −0.63 per year. TBA degradation rates were estimated for 110 wells (21 sites) and ranged from −4.9 per year to 1.71 per year, with a median value of −0.52 per year.

(2) Median point attenuation rates in wells at each site: Site-wide attenuation rates obtained by calculating the median attenuation rate for individual wells at each site are shown in Fig. 8(b). Attenuation rates ranged between −0.12 and −2.9 per year (median = −0.65 per year) for benzene, −2.7 and 0.01 per year (median = −0.69 per year) for MTBE, and −2.94 and 0.025 per year (median = −0.63 per year) for TBA. These median attenuation values are comparable, but slightly faster (i.e., more negative), than the values determined for each chemical on the basis the full well population [see Fig. 7(a)].

In summary, concentration trends in individual wells and on a site-wide basis indicate that the point attenuation rates of benzene, MTBE, and TBA are similar

Overall Plume Attenuation Rates Based on Trend of Median and Maximum Concentrations among All Sites

As an alternative measure of the relative behavior of benzene, MTBE, and TBA in groundwater, the overall concentration trend for each constituent among the full population of sites was characterized as the change in the median and maximum concentrations versus time among all sites, as shown on Figs. 9(a) and 9(b) and discussed below.

(1) Reduction in overall median concentration versus time for full site population: The median concentrations of benzene, MTBE, and TBA in groundwater for the full site population all decreased significantly over the past 10 years. As indicated in Fig. 8(a), the overall attenuation rates (C versus t) exhibited by these median concentration values over the past 10 years are −0.20 per year, −0.47 per year, and −0.27 per year for benzene, MTBE, and TBA, respectively, corresponding to half lives of 3.4, 1.5, and 2.5 years.

(2) Reduction in maximum concentration versus time for full site population: Similar to the median values, the maximum concentrations of benzene, MTBE, and TBA in groundwater for this site population also decreased significantly over the past 10 years.

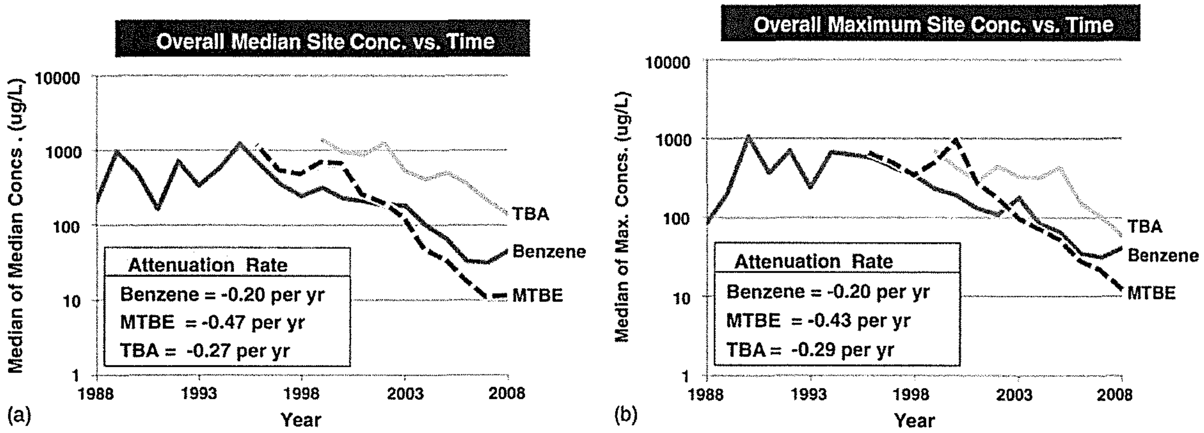

Fig. 8. Trend in site-wide median and maximum plume Concentrations versus time

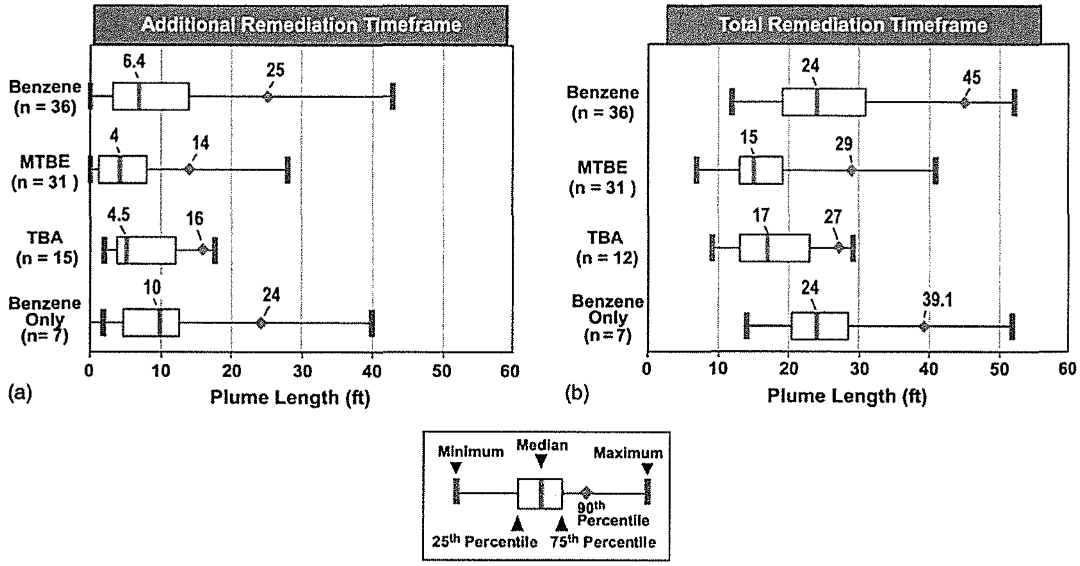

Fig. 9. Time to Remediation for Sites with Stable or Shrinking Plumes ("Benzene Only" refers to those sites where only benzene, not MTBE or TBA, exceeded the applicable remediation goal.)

As indicated in Fig. 8(b), the overall attenuation rates (C versus t) exhibited by these maximum concentration values over the past 10 years are −0.20 per year, −0.43 per year, and −0.29 per year for benzene, MTBE, and TBA, respectively, corresponding to half lives of 3.5, 1.6, and 2.4 years.

In summary, when evaluated on the basis of the full site population, both the median and maximum MTBE concentrations measured in groundwater are observed to decrease at a faster rate than the median and maximum concentrations of benzene. The faster attenuation rate observed for MTBE relative to benzene may reflect the effect of (1) the discontinued use of MTBE in the past decade, as a result of which unlike benzene, additional releases of MTBE cannot occur at active UST sites and/or (2) the much higher solubility of MTBE, compared with benzene, which can result in a more rapid rate of dissolution and depletion of MTBE from the source, eventually resulting in lower contributions of MTBE from the source to the plume, relative to benzene.

The median and maximum TBA concentrations observed for this site population are generally higher than either MTBE or benzene. In addition, TBA exhibits an overall average attenuation rate that is slower than MTBE. These observations are consistent with a temporary build-up of TBA, as a biodegradation product of MTBE, and limited biodegradation of TBA within the more concentrated portions of the plume in which electron acceptors were depleted by preferential biodegradation of BTEX and MTBE.

Effect of Active Groundwater Remediation on Plume Attenuation Rates

To evaluate the influence of active remediation on plume concentration trends, attenuation rates at sites at which active groundwater remediation and/or LNAPL recovery were conducted were compared with attenuation rates at those sites that were managed by MNA only. Table 1 summarizes the median attenuation rates determined for sites classified as: (1) MNA only, (2) NAPL recovery only, (3) groundwater remedy only, or (4) groundwater remedy plus NAPL recovery, on the basis of whether such actions were conducted for any period of time in the site history.

Student's t-tests (two-sided) comparing these four groups found that, for all three plume constituents, no statistically significant difference existed between the attenuation rates observed between (1) MNA-only sites versus groundwater remedy only sites (groups 1 and 3 in Table 1; p-value range for the three compounds = 0.10–0.43) or between (2) the combined population of MNA-only plus NAPL recovery only sites (groups 1 and 2 in Table 1) versus the combined population of groundwater remedy only and groundwater remedy with NAPL recovery sites (groups 3 and 4 in Table 1) (p-value range for the three compounds = 0.33–0.62). This analysis indicates that, for this set of sites, active groundwater remedies did not serve to measurably alter the rate of attenuation of plume concentrations versus time for the benzene, MTBE, or TBA. Rather, the fact that groundwater remedy only sites display attenuation rates comparable with those of MNA-only sites suggests that

Table 1. Comparison of Attenuation Rates of Median Plume Concentration versus Time for Different Remedial Action Conditions

	Benzene		MTBE		TBA	
Groundwater remediation method	No. of Sites	Median attenuation rate (1/yr)	No. of sites	Median attenuation rate (1/yr)	No. of sites	Median attenuation rate (1/yr)
1) MNA only	7	−0.20	6	−0.56	3	−0.23
2) NAPL recovery only	9	−0.13	9	−0.42	7	−0.18
3) Groundwater remedy only	13	−0.27	14	−0.47	12	−0.24
4) Groundwater remedy with NAPL recovery	13	−0.09	13	−0.46	11	−0.06

natural attenuation is likely the dominant attenuation mechanism for this population of sites. This observation is supported by the overall trend of TBA and MTBE concentrations across the full population of sites (see point 5 above). The presence of TBA in groundwater at concentrations greater than MTBE similarly indicates that biodegradation of MTBE (i.e., conversion to TBA) is the dominant mass removal mechanism for MTBE and that this natural attenuation process is more significant than active remediation for this site population.

The finding that groundwater plumes at sites managed by MNA only versus sites managed by active groundwater remediation are comparable is consistent with prior investigations of large populations of BTEX plumes (benzene, ethylbenzene, toluene, and xylene), as reported in Newell and Connor (1998). Specifically, studies by Rice et al. (1995) of 208 BTEX plumes in California and by Mace et al. (1997) of 93 BTEX plumes in Texas found no statistical difference in plume lengths between active groundwater remediation sites and MNA only sites.

In summary, the attenuation rates of the median concentrations of the three plume constituents are equivalent for sites in which active groundwater remediation was conducted versus sites in which only MNA was applied. In the absence of more detailed information regarding the remediation activities at each of the sites in this study, particularly with regard to the mass of constituents removed or destroyed, and a comparison of plume conditions before and after the remedy, a degree of uncertainty in this analysis is recognized with respect to the effect of remediation on plume conditions. For example, remediation efforts that remove a significant portion of the source mass from the groundwater can certainly serve to reduce the maximum plume size and increase the rate of plume shrinkage. However, at face value, the similarity of the attenuation rates observed at actively remediated versus nonactively remediated sites suggests that natural attenuation of benzene, MTBE, and TBA may be the principal mechanism of mass removal for this population of plumes.

Additional and Total Remediation Timeframe

For sites with stable or shrinking plumes, which are amenable to calculation of point attenuation rates (C versus t), the average attenuation rates calculated for each site (see item 4b above) were used to calculate the additional time necessary for the site to meet the applicable groundwater remediation goal [see Fig. 9(a)]. The additional remediation timeframe was estimated to range from 0 to 43 years for benzene (median = 6.4 years for 36 sites), 0 to 28 years for MTBE (median = 4 years for 31 sites), and 2 to 18 years for TBA (median = 4.5 years for 15 sites).

For this same population of sites, the total remediation timeframe was determined as the sum of the additional remediation timeframe plus the number of years since monitoring first began on the site. The total remediation timeframe was estimated to range from 12 to 52 years for benzene (median = 24 years for 36 sites), 7 to 41 years for MTBE (median = 15 years for 31 sites), and 9 to 29 years for TBA [median = 17 years for 15 sites; see Fig. 9(b)]. For sites with MTBE and/or benzene plumes, the combined total timeframe to reach applicable remediation goals is within the range 16 to 53 years, with a median timeframe of 28 years. For sites at which only benzene ever exceeded the applicable remediation goal (i.e., no exceedance for either MTBE or TBA), the total remediation timeframe was estimated to be from 14 to 52 years (median = 24 years; 7 sites).

In summary, evaluation of the additional and total timeframe required to achieve remediation goals again shows benzene and MTBE plumes to exhibit similar behavior. Note that the total remediation timeframes for benzene and/or MTBE plumes combined (range of 16 to 53 years, with a median timeframe of 28 years) are comparable to the total remediation timeframes for sites at which groundwater impacts are limited to the presence of benzene only, with no MTBE effects above the applicable remediation goal (range of 14 to 52 years, with a median of 24 years). These results indicate that MTBE plumes are not recalcitrant in comparison to benzene plumes; in contrast, they can be expected to attenuate within the same general timeframe. Indeed, as suggested by the data in this study, at many sites, MTBE plumes may be observed to reach remediation goals more quickly than the benzene plume.

Comparison to Previous Studies

Earlier studies predicted that, in comparison to non-MTBE gasoline, releases of MTBE-containing gasoline from UST sites would result in relatively long plumes and much longer-term effects on groundwater resources (Fogg et al. 1998; Odencrantz 1998; Weaver and Small 2002). However, the results of the evaluation of gasoline plume behavior at 48 sites located in diverse hydrogeologic settings across the nation indicate that at a majority of UST sites that were monitored for five or more years: (1) the MTBE concentrations in groundwater significantly diminished over time, (2) MTBE plume lengths and stability conditions are comparable to benzene plumes, and (3) MTBE plume attenuation is on track to achieve remedial goals within a timeframe comparable to or less than that of benzene plumes. These findings are consistent with other studies that examined monitoring data for large populations of UST sites across the nation and found that the spatial extent and duration of MTBE effects on groundwater resources is much less than previously anticipated (Mace and Choi 1998; Reid et al. 1999; Shorr and Rifai 2002; Rifai et al. 2003; Wilson et al. 2003; Shih et al. 2004; Stevens et al. 2006). Review of our specific findings with regard to those of previous studies is summarized in Table 2 and discussed in further detail below.

1. Plume stability: The percentage of stable or shrinking MTBE plumes at the 41 sites evaluated in this study (90%) is toward the upper end of the range of values (50 to 96%) published in previous studies for a total of 81 sites evaluated in Texas in 2002 (Shorr and Rifai 2002) and in Florida in 1999 (Reid et al. 1999). These results suggest that, given the longer monitoring periods that were the focus of the current study and the greater passage of time since the release, a larger percentage of MTBE plumes will attenuate to a stable or shrinking condition.
2. Plume length: The median MTBE plume length determined in this study (adjusted upper-end median of 140 feet) is on the lower end of the range of median lengths (140 feet to 178 feet) reported in earlier studies (Mace and Choi 1998; Wilson et al. 2003; Reid et al. 1999). Again, this shorter median plume length may reflect the longer monitoring periods for the sites included in this study, which is consistent with continued attenuation of MTBE plume lengths over time.
3. Point attenuation rate: The median attenuation rate for MTBE in groundwater (–0.63 per year) reported for the sites include in this study is faster than the attenuation rate values published in previous studies (median of –0.35 per year) for MTBE-affected sites undergoing natural attenuation only (Schirmer et al. 1999; Wilson and Kolhatkar 2002; Hansen et al. 2003; Rifai et al. 2003; EPA 2005). The faster MTBE attenuation rates observed in this study may reflect the effect of the longer monitoring period, which may provide a more accurate estimate for attenuation rates for compounds, such as MTBE, that entail longer periods for acclimation of the in situ bacterial population.

Table 2. MTBE Plume Characteristics Reported in the Current Study versus that Reported in Literature

	Results for MTBE plumes					
	Current study		Prior studies of data for multiple plumes			
MTBE plume characteristic	No. of sites	Value	No. of sites	Value	Reference	Comments
Percent of stable or shrinking plume	41	90%	81	50% to 96%	(Shorr and Rifai 2002; Reid et al. 1999)	Results fit within the range of previous findings, but indicate higher % of stable/ shrinking plumes.
Plume length (feet)	35	Median = 140 ft[a]	356	Median = 140–178 ft	(Mace and Choi 1998; Wilson et al. 2003; Reid et al. 1999)	The study finds median MTBE plume length to be at lower end of range in prior studies.
Point attenuation rate (per year)	33	-3.6 to 0.29 (Median = -0.63)	100[b]	-1.2 to -0.15 (Median = -0.35)	(Schirmer et al. 1999; Wilson and Kolhatkar 2002; Hansen et al. 2003; EPA 2005; Rifai et al. 2003)	The study finds MTBE attenuation rates to be faster than previous studies.

[a] Table shows the adjusted median plume length for sites at which plume lengths were either measured, estimated, or considered indeterminate.
[b] Results reported from MNA-only sites.

In addition, given the discontinued use of MTBE as a fuel additive, additional releases of MTBE can no longer occur at active UST sites; therefore, in the absence of such additional source contributions, faster attenuation rates are likely to be observed within the population of existing MTBE plumes (Stevens 2006). Furthermore, the higher solubility of MTBE compared with benzene may contribute to more rapid dissolution and depletion of MTBE from the source, resulting in larger reductions in source contributions of MTBE to the plume over the long term.

Conclusions

This study addresses the characteristics of benzene, MTBE, and TBA plumes in groundwater for a population of 48 retail service station sites, specifically in terms of plume length, plume stability condition, concentration reduction trends over time, attenuation rates, and the timeframe within which natural attenuation achieved remedial goals for each constituent. The goal of this evaluation was to characterize plume behavior as observed across a variety of hydrogeologic settings on the basis of detailed groundwater monitoring records, rather than to define the site-specific factors controlling plume behavior. The groundwater monitoring data analyzed in this study confirm that, over the long term for this site population, the behavior of MTBE plumes in groundwater is similar to that of benzene plumes with respect to current plume lengths and plume stability trends. However, overall MTBE concentrations are decreasing more quickly than benzene, and may, on average, reach the applicable remediation goals more quickly than benzene plumes. The faster attenuation of MTBE plumes compared with benzene is consistent with the discontinued use of MTBE as a fuel additive.

TBA plumes were also found to be comparable to benzene and MTBE plumes in terms of plume length. However, whereas most TBA plumes are stable or shrinking, the percentage of TBA plumes currently stable or shrinking (68%) is less than that for benzene plumes (95%) and MTBE plumes (90%), likely reflecting the temporary build-up of TBA concentrations in groundwater attributable to MTBE biodegradation. Nevertheless, overall trends for the median and maximum concentrations of TBA in groundwater at these sites indicate that TBA is attenuating at rates somewhat faster than benzene and can therefore be expected diminish to applicable remediation goals in a similar timeframe as the other gasoline constituents.

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