Groundwater

Review Paper/

Review of Quantitative Surveys of the Length and Stability of MTBE, TBA, and Benzene Plumes in Groundwater at UST Sites

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Abstract

Quantitative information regarding the length and stability condition of groundwater plumes of benzene, methyl tert-butyl ether (MTBE), and tert-butyl alcohol (TBA) has been compiled from thousands of underground storage tank (UST) sites in the United States where gasoline fuel releases have occurred. This paper presents a review and summary of 13 published scientific surveys, of which 10 address benzene and/or MTBE plumes only, and 3 address benzene, MTBE, and TBA plumes. These data show the observed lengths of benzene and MTBE plumes to be relatively consistent among various regions and hydrogeologic settings, with median lengths at a delineation limit of 10 μg/L falling into relatively narrow ranges from 101 to 185 feet for benzene and 110 to 178 feet for MTBE. The observed statistical distributions of MTBE and benzene plumes show the two plume types to be of comparable lengths, with 90th percentile MTBE plume lengths moderately exceeding benzene plume lengths by 16% at a 10-μg/L delineation limit (400 feet vs. 345 feet) and 25% at a 5-μg/L delineation limit (530 feet vs. 425 feet). Stability analyses for benzene and MTBE plumes found 94 and 93% of these plumes, respectively, to be in a nonexpanding condition, and over 91% of individual monitoring wells to exhibit nonincreasing concentration trends. Three published studies addressing TBA found TBA plumes to be of comparable length to MTBE and benzene plumes, with 86% of wells in one study showing nonincreasing concentration trends.

Introduction

Over the past two decades, thousands of underground storage tank (UST) sites across the United States have been investigated to assess the potential impacts of gasoline fuel leaks on the underlying soil and groundwater. This experience has generated extensive information regarding the nature and extent of groundwater plumes containing benzene, methyl tert-butyl ether (MTBE), and tert-butyl alcohol (TBA). In the 1990s, when regulations required that gasolines be blended with oxygenate additives like MTBE for more efficient combustion, some researchers predicted that, in the event of a gasoline release to groundwater, MTBE would form much longer groundwater plumes compared to benzene (Fogg et al. 1998; Odencrantz 1998; Weaver and Small 2002). These authors based their predictions upon considerations that (1) MTBE is more soluble and less sorptive than benzene and could therefore travel farther than benzene in groundwater, in the absence of other attenuation mechanisms; and (2) MTBE, unlike benzene, was suspected to be relatively resistant to biodegradation by native soil bacteria (Yeh and Novak 1991; Suflita and Mormile 1993; Mormile et al. 1994).

These predictions were initially supported by the discovery of a few exceptionally long MTBE plumes extending thousands of feet downgradient of the release

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point, such as in Long Island, New York (Weaver et al. 1996, 1999). In contrast to these few exceptionally long plumes, several studies conducted in the mid-1990s that compiled information from numerous UST sites found the measured lengths of benzene and MTBE plumes to be comparable (Happel et al. 1998; Mace and Choi 1998). However, some authors questioned whether these results were reliable, postulating that younger MTBE plumes could be continuing to expand while older benzene plumes might be stable or diminishing in size, and/or noting that proper delineation of plume lengths could be hampered by diving plume conditions or other limitations (Happel et al. 1998; Mace and Choi 1998; Shih et al. 2004).

Subsequent scientific studies have improved our understanding of the lifecycle of contaminant plumes and the behavior of gasoline additives in groundwater. Specifically, field and laboratory investigations have found MTBE to biodegrade in groundwater under both aerobic and anaerobic conditions (Mackay et al. 2001, 2007; Wilson et al. 2002; Gray et al. 2002; McKelvie et al. 2007a). Published studies conducted from 1995 to 2013 have compiled field data from thousands of UST sites across the country, providing information on the measured lengths of MTBE and benzene plumes in groundwater and/or the observed plume stability condition (Rice et al. 1995; Buscheck et al. 1996; Mace et al. 1997; Happel et al. 1998; Reid et al. 1999; Reisinger et al. 2000; Shorr and Rifai 2002; Wilson 2003; Rifai and Rixey 2004; Shih et al. 2004; Stevens et al. 2006; Tarr and Galonski 2007; Kamath et al. 2012). In addition, three studies have addressed the behavior of TBA plumes found in conjunction with MTBE gasoline releases (Shih et al. 2004; Kamath et al. 2012; McHugh et al. 2013).

Purpose of Review

In this paper, we have reviewed the results of 13 published studies of multiple plumes to characterize the statistical distribution of plume lengths, plume stability conditions, and concentration trends for benzene, MTBE, and TBA plumes at UST sites. These studies have applied a variety of technical criteria and methodologies to achieve a representative measurement of plume lengths and stability conditions at retail gasoline sites. In total, the studies provide quantitative data on over 550 MTBE plumes and over 1300 benzene plumes at retail gasoline sites in a variety of hydrogeologic settings.

This review paper updates prior publications that compiled information on large populations of benzene and MTBE plumes (Newell and Connor 1998) by incorporating the results of additional multi-plume studies conducted over the past 15 years. In addition, this study incorporates the results of three studies that have addressed TBA plume behavior in addition to benzene and MTBE (Shih et al. 2004; Kamath et al. 2012; McHugh et al. 2013). This paper describes the methodology employed to review and compile these data, presents statistical summaries of benzene, MTBE, and TBA plume characteristics, and addresses the significance and limitations of these data.

Compilation of the data from these 13 separate studies is intended to provide a more complete understanding of plume behavior across multiple regions, as well as summary statistics on the observed length and stability condition of these plumes. This review serves to compile information generated over two decades of scientific investigation so as to provide the reader the benefit of the accumulated knowledge and weight of evidence that could not be obtained from the individual studies on their own.

Compilation of Data from Published Studies

We have surveyed the published literature to identify prior studies that have compiled quantitative data on groundwater plume conditions at multiple UST sites in the United States. Table 1 lists 13 studies that provide quantitative information and statistical summaries regarding the lengths and/or stability conditions of benzene, MTBE, and/or TBA groundwater plumes. Appendix S1 includes summary data from each paper tabulated as the basis for this paper.

Technical Specifications of Quantitative Surveys of Plume Characteristics

Each of the studies compiled in this paper has employed one or more technical criteria to obtain a representative sampling of plume characteristics from among existing groundwater monitoring records at UST sites. Key considerations include the following:

1. *Nature of Release.* These studies provide information on plume conditions associated with gasoline fuel releases from UST systems, principally retail fuel marketing facilities. Plumes associated with other potential sources of release (pipelines, refineries, tank farms, truck spills, etc.) or materials (diesel fuel, bulk additives, etc.) were not included in these databases.
2. *Survey of Multiple Site Locations.* Each of the studies provides quantitative data on multiple benzene, MTBE, and/or TBA plumes. Individual studies on plume lengths include 22 to 289 sites per study. Studies on plume stability conditions include 34 to 271 sites per study, with one study addressing the overall plume concentration trends observed at over 4000 UST sites in California (McHugh et al. 2013).
3. *Duration of Groundwater Monitoring History.* A number of the studies selected sites with longer-term monitoring periods so as establish plume trends with less uncertainty associated with seasonal fluctuations, sampling variability, and attenuation rates for compounds, such as MTBE, which have been observed to require longer acclimation periods for biodegradation. For those studies that specified minimum monitoring periods, the minimum monitoring periods required exceeded one year in duration, with most of the studies requiring three or more years.
4. *Number of Groundwater Monitoring Points.* For most of the studies reviewed, plume characterization was based upon a minimum number of three to eight monitoring points per site to define the plume length or

Table 1
Summary of Studies on Plume Length and Plume Stability Conditions Based upon Data from Multiple UST Sites

Study	State	No. of Sites Meeting Minimum Specifications	Minimum Specifications for Evaluation Sites	Plume Length Reported?	M, B in Same Wells?	Plume Stability Condition Evaluated?	
						Length Versus Time	GW Conc. Trend
1. Rice et al. (1995)	CA	271	8 events; 6 wells	B (271 sites)	—	B (271 sites)	B (271 sites)
2. Buscheck et al. (1996)	CA	119	NR	BTEX/Benzene (62 sites)[1]	—	—	BTEX (119 sites)
3. Mace et al. (1997)	TX	227	6 wells	B (217 sites)[2]	—	B (217 sites)	B (227 sites)
4. Happel et al. (1998)	CA	63	1 sampling event; 8 wells	M (50 sites), B (50 sites)[3]	Yes (43 sites)	—	—
5. Mace and Choi (1998)	TX	289	Three events (1995–1997)	M (89 sites[4]), B (289 sites)	—	M, B (20 sites)[5]	M (471 wells)
6. Reid et al. (1999), Reisinger et al. (2000)	FL	55	3 years; Minimum 3 wells with detections MTBE	M (55 sites), B (54 sites)	Yes	M (45 sites)	—
7. Shorr and Rifai (2002), Rifai et al. (2003), Rifai and Rixey (2004)	TX	36	3 years; Minimum 6 wells; Minimum 3 years MTBE data	M (36 sites), B (36 sites)	Yes	M (36 sites), B (36 sites)	M (1074 wells), B (1206 wells)[6]
8. Wilson (2003)	SC	212	NR	M (212 sites), BTEX (212 sites)	Yes	—	—
9. Shih et al. (2004)	CA	96	1 year; sufficient wells; proper lab QA/QC	M (96 sites), B (95 sites), TBA (86 sites)	Yes	M (96 sites), B (94 sites), TBA (86 sites)[7]	—
10. Stevens et al. (2006)	CT	22	4 years; active UST; no NAPL; consistent monitoring program; no active remediation	—	—	—	M (83 wells)
11. Tarr and Galonski (2007)	NH	25	M detections	—	—	—	M (78 wells)
12. Kamath et al. (2012)	CA, NJ, AK, OR, NV	48	Min. 6 wells	M (35 sites), B (34 sites), TBA (22 sites)	Yes, including TBA	M (41 sites), B (42 sites), TBA (34 sites)	M (42 sites, 306 wells), B (43 sites, 288 wells), TBA (34 sites, 241 wells)
13. McHugh et al. (2013)	CA	>4000	2001 to 2011	—	—	—	M (4190 sites) B (4404 sites), TBA (3675 sites)
Total	—	—	—	M (573 sites), B (1320 sites), TBA (108 sites)	474 sites	M (238 sites), B (680 sites), TBA (120 sites)	—

M = Methyl tert-butyl ether (MTBE); B = Benzene; BTEX = Benzene, toluene, ethylbenzene, and xylenes; TBA = tert-butyl alcohol; NR = not reported; — = not analyzed; NAPL = nonaqueous phase liquid; QA/QC = quality assurance/quality control; UST = underground storage tank.

[1] Buscheck et al. (1996) reported the percentage of sites with BTEX plume lengths less than 50 feet, between 50 and 100 feet, between 100 and 200 feet, and greater than 200 feet. The terms BTEX and benzene appear to be used interchangeably within this study.

[2] Mace and Choi (1998) also presented benzene plume length data, and these data were used to compare with MTBE; Mace et al. (1997) benzene plume length results are not presented in this paper to prevent double-counting the same dataset.

[3] Benzene plume lengths were estimated based on a 1-µg/L contour limit, inconsistent with the other studies, and therefore could not be used for weighted mean calculations in our paper.

[4] Mace and Choi (1998) estimated plume lengths at 99 sites, but 10 of these sites had plume lengths of 0 feet.

[5] Mace and Choi (1998) estimated plume behavior (i.e., plume stability) over time at 20 sites based on plume lengths measured at three different events but did not present the full results of their analysis, and their incomplete results are not analyzed in this paper.

[6] Shorr and Rifai (2002) only presented the number of wells with near zero or decreasing trends, and their plume stability results are not aggregated in this paper because relative percentages of wells in each trend category were not specified.

[7] Shih et al. (2004) aggregated the plume length dataset before statistical analysis of plume stability and concluded that while the plume length decreased for MTBE and increased for benzene and TBA, these results were not statistically significant at a 95% confidence interval.

stability condition, with most of these studies requiring six or more monitoring points. The actual number of monitoring wells employed at most sites exceeded this minimum specification, with reported average numbers of monitoring points ranging from approximately 4 to 17 per site.

Methodologies for Characterization of Plume Length

The studies reviewed for this paper evaluated plume length based upon a site-by-site evaluation of groundwater monitoring data. Plume lengths were determined based upon measured site data by either of two methods: (1) hand-contouring of the measured concentrations on a scaled map of the sampling locations to the designated concentration limit, or (2) using an empirical or analytical method to estimate the plume length when the existing monitoring well network did not extend downgradient to the specified plume delineation limit. We refer the reader to the individual studies for method particulars.

The prior studies have employed a variety of concentration limits for the purpose of delineating plume length. In our review, based upon consideration of the action levels employed under many state regulatory programs in the United States, we have focused on MTBE and benzene plumes that have been delineated to a 5 or 10 µg/L (micrograms per liter) concentration limit. For benzene, many state agencies employ a 5 µg/L action level (corresponding to the Federal Primary Maximum Contaminant Level [MCL] for benzene in drinking water) for remediation of groundwater that is considered a potential drinking water source. MTBE action levels are generally higher and more variable among state agencies, with levels as low as 5 µg/L applied in California (Secondary MCL for MTBE; CDPH 2006). Evaluation of the plumes delineated to concentration limits of 5 or 10 µg/L provides a conservative basis for characterization of plumes subject to remedial action, as a number of states employ less stringent groundwater cleanup criteria, particularly for MTBE. TBA plumes were evaluated at a 10 µg/L (Shih et al. 2004) and 12 µg/L (Kamath et al. 2012) limit, consistent with California's drinking water notification level of 12 µg/L. Although these contour limits were not identical, the two datasets were combined in this study at an assumed level of 10 µg/L to increase the number of TBA sites, which have been evaluated in far fewer studies than either benzene or MTBE.

Methodologies for Classification of Plume Stability Conditions

As defined in prior publications (Rice et al. 1995; Newell and Connor 1998; ASTM 2010), the stability condition of an affected groundwater plume can be characterized according to the following stages (Figure 1):

1. *Expanding Plume*: The plume length and/or concentrations are increasing over time. Commonly observed immediately after the spill material reaches the groundwater and the dissolved chemicals are transported by moving groundwater.
2. *Stable/No Trend Plume*: The plume length and/or concentrations are not changing over time, indicating that the rate at which the dissolved chemical mass is entering the groundwater is balanced by natural attenuation mechanisms, such as dilution, dispersion, sorption, and biodegradation. "Stable" and "No Trend" were considered equivalent designations in a number of the studies. For those papers that distinguished between stable and no trend plumes, both designations indicate the plume concentration to be neither decreasing nor increasing with time; however, the "No Trend" designation entails a higher amplitude of variation (i.e., higher coefficient of variation) than the "Stable" designation.
3. *Shrinking Plume*: The plume length and/or concentrations are diminishing over time, indicating that the rate of mass release from the source area has reduced to the extent that the attenuation factors remove and disperse mass faster than it is entering the groundwater system.
4. *Non-Detect or Exhausted Plume*: In some cases, the affected groundwater zone may diminish to non-detectable levels in the groundwater, while at other sites, the process may slow or terminate in an "exhausted" condition, with trace concentrations of gasoline components remaining near the original source location.

At a given site, measurements can be conducted to determine if a plume is in an expanding, stable, shrinking, or exhausted condition (ASTM 2010). The plume stability condition can be characterized either on the *trend of the plume length* over time or the *trend of plume concentrations* over time in individual monitoring wells.

In the various studies identified on Table 1, the stability of the plume length over time was determined either by: (1) evaluating plume contour maps at different times to determine changes in the length of the plume, or (2) conducting statistical trend analyses on the concentrations measured at monitoring wells, typically located at the downgradient toe of the plume. For the purpose of analysis of plume concentration trends over time, various visual and statistical methods were employed to categorize trends as increasing, decreasing, or stable; we refer the reader to the individual studies for method particulars. While the reports used a variety of methods to characterize plume stability, the similarity of their results points to the consistency of MTBE, benzene, and TBA plume behavior across the various published studies and supports aggregating these results, as done in our study.

Statistical Review of Published Studies

To facilitate comparison of the typical lengths of MTBE, benzene, and TBA plumes at UST sites, overall median and 90th percentile plume lengths have been estimated as the weighted mean of the median and 90th percentile values reported in the individual studies. This calculation is based upon the understanding that, for sufficiently large datasets, order statistics, such as the median and 90th percentile values, are normally

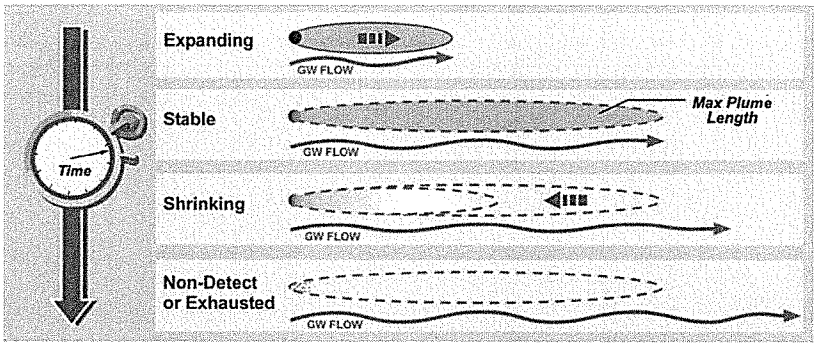

Figure 1. Schematic of groundwater plume stages at a typical UST site following termination of a spill or leak.

distributed, even if the underlying populations are not normally distributed. A weighted mean, based on the number of samples, has been employed to reduce the influence of smaller sample populations, which may exhibit greater variability in order statistics than larger sample populations. In other words, studies with more sites were weighted more heavily than studies with fewer sites. Similarly, the weighted mean approach was utilized to combine the results of the plume stability and concentration trend analyses.

The McHugh et al. (2013) study considered over 4000 UST sites to evaluate the overall trends of the maximum concentrations of MTBE, TBA, and benzene in groundwater over time. They did not address site-specific plume length or stability conditions, but provided important information regarding the net change in chemical concentrations over time in groundwater across these sites. Given the large number of sites they evaluated compared to the other published studies we reviewed, these results were not combined into the concentration trend summary statistics because they would overwhelm the weighted mean calculations; however, the results of McHugh et al. (2013) are compared with the summary statistics in this paper.

Limitations of These Studies

The authors of the various studies have identified possible limitations in their databases and, when feasible, have employed steps to mitigate the effects of these limitations on their findings. For example, a number of the studies note that, at many UST sites, the affected groundwater plumes are not fully delineated due to access restrictions or other limitations on the number and placement of groundwater sampling points. In addition, some authors note that, if the plume stability condition is not considered, comparison of older, stable plume lengths to younger, expanding plumes could be misleading, as the expanding plumes will not have achieved full length. Some authors also suggest that differences in MTBE and benzene plume lengths could reflect the effect of variable site conditions if the MTBE and benzene plumes are from different sites with distinctly different distributions of key attenuation parameters.

These limitations have been addressed by the authors of the 13 plume studies in a variety of manners. In some studies, plume lengths have been evaluated only for plumes with full delineation, based on a specified minimum number of monitoring points. In other studies, the maximum downgradient extent of the plume has been estimated based upon extrapolation of measured monitoring points, using the method described by Freeze and Cherry (1979) or Newell et al. (2002). Kamath et al. (2012) found this plume length estimation method to provide a reasonably conservative match to measured plume lengths on sites where both measurement and estimation methods were applied. Furthermore, six of the 10 studies that evaluate plume length compare benzene and MTBE plumes lengths from the same sites under the same hydrogeologic conditions.

In addition, 11 of the 13 studies have addressed the stability condition of the plumes, providing a basis for determining whether variations in plume age and associated stability condition (e.g., young expanding plume vs. older shrinking plume) could account for observed differences in the lengths of MTBE and benzene plumes. The vast majority of both benzene and MTBE plumes were found to be in a nonexpanding condition, showing that the concern of young versus old plumes is not a factor for plume length. The McHugh et al. (2013) study relied upon the maximum annual concentration of each plume constituent as a conservative basis to track plume concentration trends over time, based upon the consideration that the maximum concentration is likely near the source and therefore less likely to be affected by the extent of plume delineation or the change in the number of monitoring wells over time.

Findings of Previous Studies

Evaluation of Plume Lengths: MTBE, Benzene, and TBA

Statistical Distribution of MTBE, Benzene, and TBA Plume Lengths

As identified in Table 1, 10 of the 13 published studies address benzene and MTBE plume lengths, providing data on a total of 391 and 132 sites for MTBE plumes at 10

and 5 µg/L delineation limits, respectively, and 826 and 165 sites for benzene plumes at 10 and 5 µg/L delineation limits, respectively. Two published studies also estimated plume lengths for TBA at a total of 108 sites (see Table S1 for tabulated values). Figure 2A and 2B provides side-by-side comparisons of the reported lengths of benzene and MTBE plumes from each of the 13 studies that evaluated plumes at a 5 and 10 µg/L plume delineation limit. Figure 3A and 3B summarize the weighted mean plume dimensions for MTBE, benzene, and TBA at delineation limits of 10 and 5 µg/L, respectively.

Consistency of MTBE and Benzene Plume Lengths Among Various Studies

The distributions of plume lengths shown in Figure 2 are relatively consistent among studies conducted in a variety of regions in the United States. For example, for plumes delineated to a 10 µg/L concentration limit (see Figure 2A), the median lengths of benzene plumes (826 sites) fall within the range of 101 to 185 feet, while the median lengths of MTBE plumes (391 sites) fall within a slightly narrower range of 110 to 178 feet (Table S1). Similarly, at this same delineation limit, the 90th percentile plume lengths range from 386 to 454 feet for MTBE (336 sites) and 261 to 480 feet for benzene (772 sites; Table S1).

The relatively narrow range of these plume length statistics across hundreds of UST sites suggests that plume lengths are consistent across a broad range of hydrogeologic settings and conditions. This observation is in agreement with prior studies that have found factors such as groundwater hydraulic conductivity and site lithology to be poor predictors of plume length among large numbers of plumes (Reid et al. 1999; Mace et al. 1997; Newell and Connor 1998; Shorr and Rifai 2002; Wilson 2003).

Comparable Lengths of MTBE and Benzene Plumes

The lengths of the benzene and MTBE plumes reported in the various studies are relatively comparable at both the median and 90th percentile levels, as illustrated by the weighted means of plume length statistics shown in Figure 3. The 90th percentile statistic is of particular interest in this regard as it incorporates the vast majority (90%) of gasoline plumes for which these data have been compiled. At a 10 µg/L delineation limit, the 90th percentile MTBE and benzene plume lengths are 400 feet (336 sites) and 345 feet (772 sites), respectively, showing MTBE plume lengths to be only 16% greater than those of benzene plumes (Figure 3A; Table S1).

At a delineation limit of 5 µg/L, the MTBE and benzene plume lengths are still found to be comparable, although with a moderately more pronounced difference; the 90th percentile MTBE (only evaluated in the Shih et al. 2004 study) and benzene plume lengths are 530 feet (96 sites) and 425 feet (165 sites), respectively, showing MTBE plumes to be 25% longer than benzene plumes (Figure 3B; Table S1). In general, the benzene plume lengths reported in the various studies are consistent with the study by Buscheck et al. (1996) that evaluated 62 UST sites in California and found that 85% of benzene plumes were less than 200 feet long. The Buscheck et al. (1996) study presented a range of plume lengths rather than a statistical distribution and thus could not be directly included in our statistical summary.

In absolute terms, the difference in these MTBE and benzene plume lengths ranges from only 55 to 105 feet (for 90th percentile plume lengths at the 10 and 5 µg/L delineation limits, respectively). The similar plume behavior of benzene and MBTE may reflect their biodegradation characteristics, as both compounds are biodegraded in aerobic groundwater and in most anaerobic geochemical settings.

Exceptionally Long Plumes

The maximum MTBE plume lengths identified in the studies addressed in this review paper generally fall in the range of 1000 to 1700 feet (see Figure 2). However, other publications have reported longer MTBE plumes (e.g., greater than 2000 feet) at individual UST sites (Weaver et al. 1996, 1999; ESTCP 2003; Thuma et al. 2001; McKelvie et al. 2007b). Consequently, while it is recognized that such exceptionally long MTBE plumes do exist, the small number of such plumes is consistent with the statistical distribution observed in the 13 studies, where MTBE plumes greater than 1400 feet in length correspond to less than 1% of the plume population. Incorporation of this small number of exceptionally long MTBE plumes into the data sets addressed in our review would not affect the weighted means of the median and 90th percentile plume lengths presented on Figure 3.

Lengths of TBA Plumes Compared to MTBE and Benzene Plumes

Two studies addressed the behavior of TBA plumes in addition to benzene and MTBE (Kamath et al. 2012; Shih et al. 2004) for a total of 108 sites. The weighted mean results from these studies (Figure 3A) indicate that the 90th percentile TBA plume length (420 feet at 10 µg/L; Table S1) is 5% greater than the 90th percentile MTBE plume determined from these and other studies. Similarly, the median TBA plume from the two studies at 10 µg/L is 15% longer than the median MTBE plume determined from a larger number of studies. However, the two studies that addressed TBA (Shih et al. 2004; Kamath et al. 2012) found TBA plume lengths to be comparable to benzene and MTBE plume lengths, with TBA plume lengths falling in between benzene and MTBE plume lengths. Shih et al. (2004) calculated 90th percentile values of the benzene, MTBE, and TBA plume lengths to be 341, 531, and 433 feet, respectively. Kamath et al. (2012) calculated the 90th percentile values of the measured and estimated plume lengths for benzene, MTBE, and TBA to be 356, 454, and 366 feet, respectively. Taken together, the aggregated results and individual studies suggest that TBA plume lengths are similar to MTBE and benzene plumes.

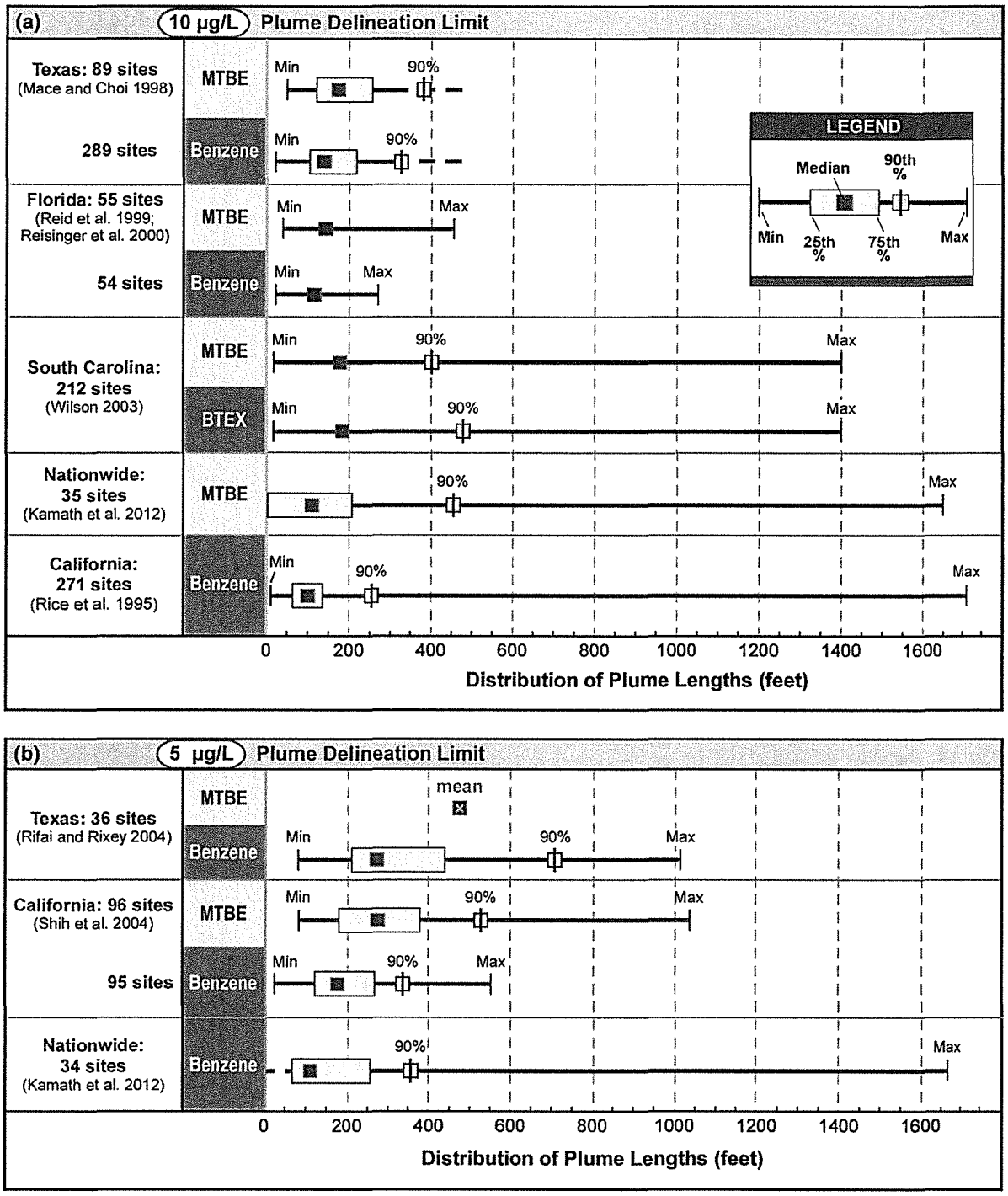

Figure 2. Summary of surveys of plume lengths in groundwater: MTBE versus benzene.

Evaluation of Plume Stability Conditions: MTBE, Benzene, and TBA

Stability Condition of Plume Lengths Over Time

Five studies have evaluated the stability of plume length over time for a combined 122 sites for MTBE plumes, 566 sites for benzene plumes, and 34 sites for TBA plumes (Reid et al. 1999; Reisinger et al. 2000; Kamath et al. 2012; Shorr and Rifai 2002; Rice et al. 1995; Mace et al. 1997). For each stability category, we have computed a weighted mean of the percentage of sites falling into that category. Table S2 reports these weighted mean values, as well as the values reported in each study, rounded to the nearest whole number for consistency.

Figure 4 compares the combined plume length trend distributions for MTBE, benzene, and TBA. These studies consistently found that the vast majority of both MTBE and benzene plume lengths are not increasing in length over time. For MTBE plumes, the percent of plume lengths found to be stable, no trend, decreasing, or

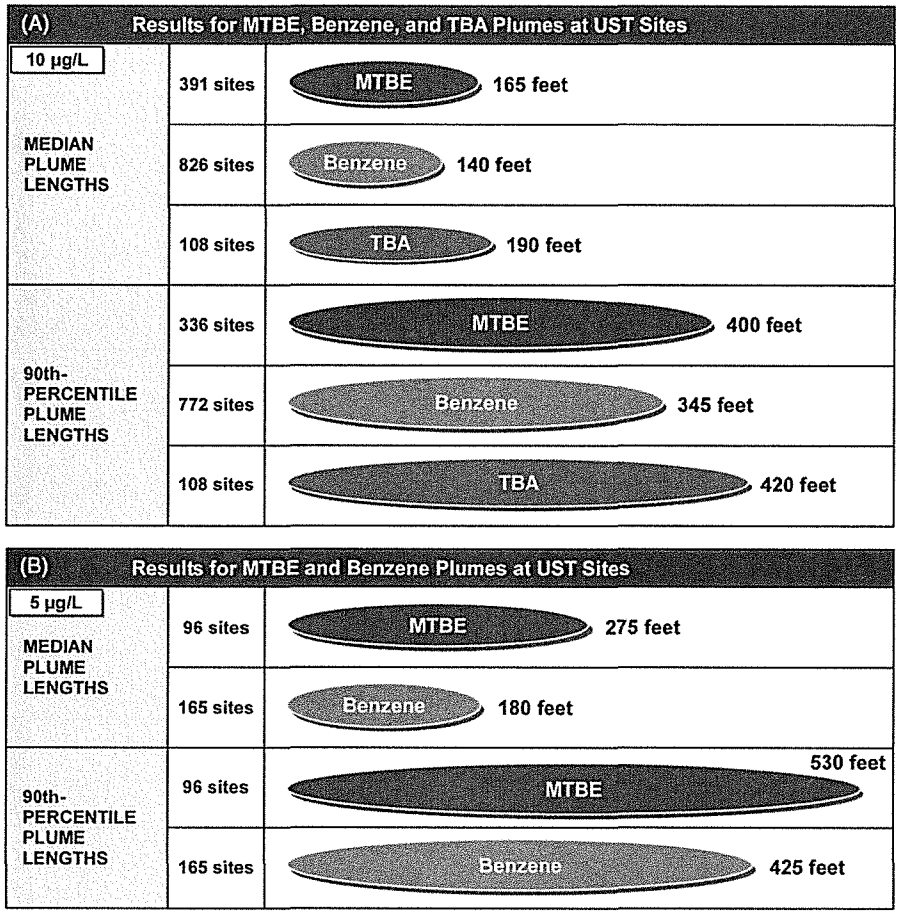

Figure 3. Weighted means of median lengths and 90th percentile lengths of MTBE, TBA, and benzene plumes. (A) Weighted means of plume lengths defined by 10 µg/L concentration limit. (B) Weighted means of plume lengths defined by 5 µg/L concentration limit. Lengths are estimated as the weighted mean of median and 90th percentile plume length values reported in various scientific surveys, rounded to the nearest 5 feet, for plumes delineated to a 10 µg/L concentration limit and 5 µg/L concentration limit. Data have been compiled for MTBE, benzene, and TBA plumes in groundwater underlying UST sites across the nation (see Table S1 for studies used to compile these summary lengths).

exhausted ranges from 90 to 96% among three studies, with the weighted mean percentage of plumes that are nonincreasing equal to 93%. Similarly, for benzene plumes, among four studies, the percent of plume lengths found to be stable, no trend, decreasing, or exhausted ranges from 92 to 97%, with the weighted mean percentage of plumes found to be nonincreasing equal to 94%. The overall percentages of plume lengths observed to be increasing over time is 6% for both MTBE plumes and benzene plumes.

The study by Kamath et al. (2012) specifically addressed the presence of detached MTBE plumes, that is, displacement of the plume mass downgradient from the original source point. They found this condition to occur at only 5% of MTBE sites (2 of 41 sites). Furthermore, these detached plumes were observed to be decreasing in area over time (Kamath et al. 2012). For the purposes of our analysis, the detached plumes were not considered as either increasing or nonincreasing.

Figure 4 also displays the trend distributions for TBA, as determined by Kamath et al. (2012). These data show that the majority of TBA plumes (68%) are stable or shrinking in length, while 26% are increasing. The percentage of nonincreasing plumes for TBA is lower than for benzene and MTBE (94 and 93%, respectively, are not increasing in length), which may reflect the temporary build-up of TBA concentrations in groundwater following biodegradation of MTBE (Kamath et al. 2012).

Concentration Trends in Individual Monitoring Wells Over Time

Seven studies have evaluated concentration trends of benzene and MTBE in individual wells over time (Mace and Choi 1998; Stevens et al. 2006; Tarr and Galonski 2007; Kamath et al. 2012; Buscheck et al. 1996; Rice et al. 1995; Mace et al. 1997), for a combined 938 wells for MTBE and 905 wells for benzene. Kamath et al. (2012) evaluated TBA concentration trends over time in 241 wells. Figure 5 shows the concentration trend distributions for MTBE, benzene, and TBA, with the percentage of plumes falling into each stability category calculated as weighted means among the seven

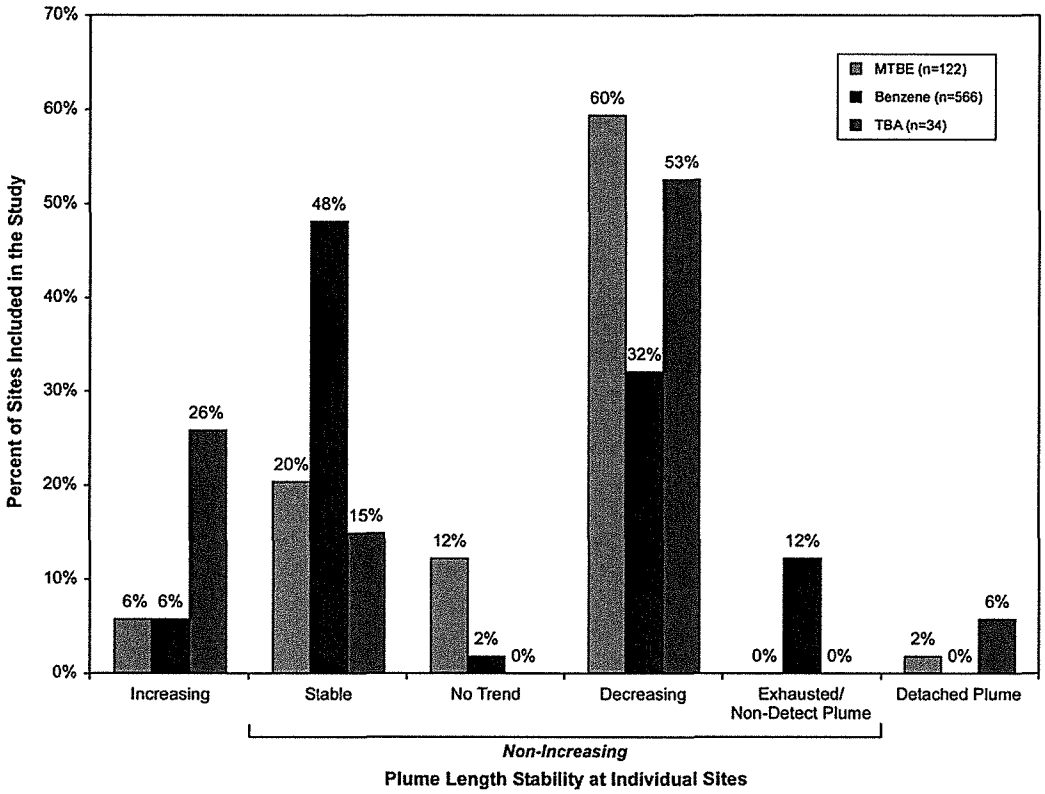

Figure 4. Comparison of plume length stability conditions for MTBE, benzene, and TBA plumes at UST sites. Data have been compiled for MTBE, benzene, and TBA plumes in groundwater underlying UST sites across the nation (see Table S2 for studies used to compile these stability percentages).

studies (see Table S3 for detailed data). In addition to these studies, McHugh et al. (2013) evaluated overall plume concentration trends for MTBE, benzene, and TBA for over 4000 sites in California. The McHugh study addressed the net change in the maximum plume concentrations at each site but did not characterize the plume stability condition per se in the same manner as the other studies; consequently, the weighted means shown on Figure 5 do not include the McHugh et al. (2013) results.

Figure 5 compares the combined distributions of well concentration trends for MTBE (938 wells), benzene (905 wells), and TBA (241 wells). As shown, MTBE and benzene again exhibit similar distributions, with the vast majority of wells showing nonincreasing concentrations over time for both MTBE (91%) and benzene (92%). However, unlike the plume length distribution, a higher percentage of wells exhibit decreasing concentrations for benzene (63%) than for MTBE (45%). Nevertheless, the combined percentage of stable, decreasing, or no trend wells is again comparable for the two compounds, corresponding to 80% of wells for MTBE and 84% of wells for benzene.

Evaluation of TBA concentration trends by Kamath et al. (2012) found stability condition distributions to be roughly comparable to those of benzene and MTBE, with 86% of the wells demonstrating nonincreasing trends. The moderately higher percentage of wells with increasing TBA concentration trends (14%, compared to 9% and 8% for MTBE and benzene, respectively) may reflect the production of TBA as a by-product of MTBE biodegradation, resulting in temporary replenishment of TBA concentrations until the MTBE source is depleted. Under this scenario, TBA concentrations in turn decrease as the MTBE source mass diminishes and the TBA itself is biodegraded.

Two studies specifically addressed MTBE plume conditions before and after the end of MTBE use as a gasoline additive in Connecticut (Stevens et al. 2006) and New Hampshire (Tarr and Galonski 2007). In both studies, in the 2 years following termination of MTBE use, the percentage of monitoring wells displaying a *decreasing* MTBE concentration trend was observed to increase. In Connecticut, Stevens et al. (2006) found that 93% of the 83 monitoring wells evaluated showed decreasing concentrations of MTBE 2 years after termination of MTBE use. By pooling the monitoring wells across 22 sites, they also determined that 55% of the sites showed a statistically significant decrease in MTBE concentrations between pre- and post-ban data (90th confidence level); only 5% (1 site) showed a statistically significant increase in MTBE concentrations. A similar study of 78 wells in New Hampshire (Tarr and Galonski 2007) reported that, after termination of MTBE use, 85% of monitoring wells exhibited decreasing concentrations, compared to decreasing concentrations at 68% of monitoring wells

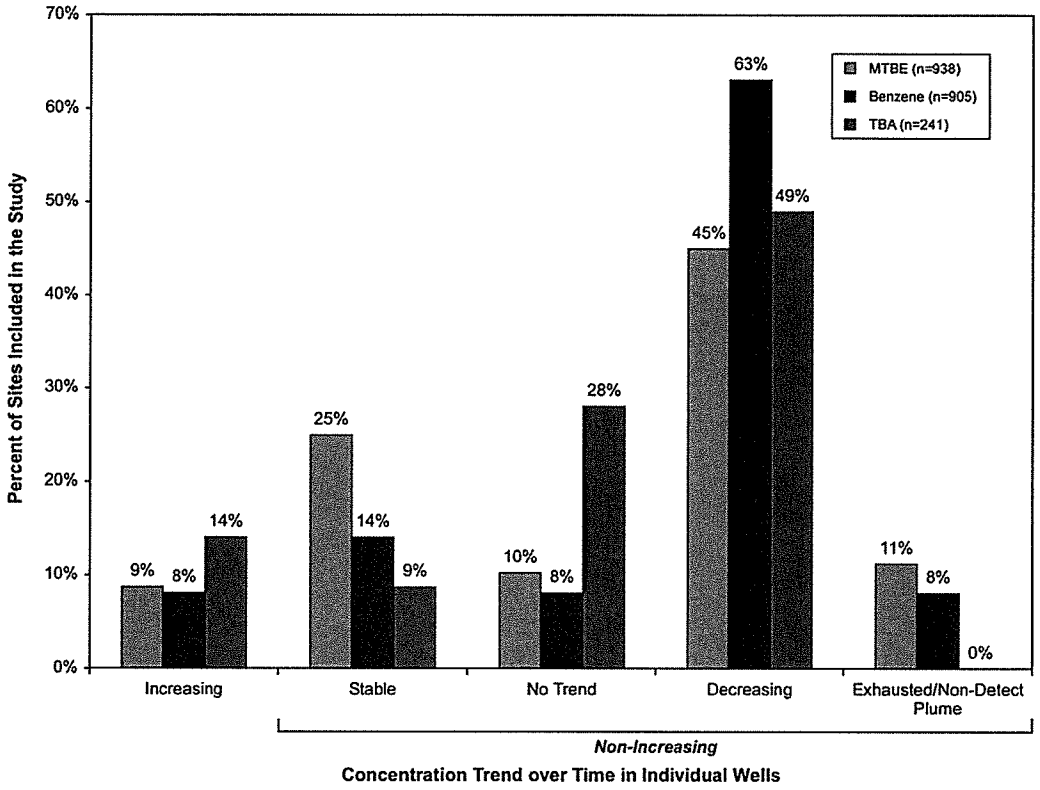

Figure 5. Comparison of concentration versus time trends for MTBE, benzene, and TBA in monitoring wells at UST sites. Data have been compiled for MTBE, benzene, and TBA concentration trends in groundwater underlying UST sites across the nation (see Table S3 for studies used to compile these concentration trends).

prior to the termination of MTBE use in gasoline. These studies demonstrated the decrease in MTBE concentrations with time following termination of MTBE use in these states.

McHugh et al. (2013) compiled data from over 4000 UST sites from the California GeoTracker database to evaluate the overall trends of benzene, MTBE, and TBA concentrations in groundwater over time. These monitoring data showed a large decrease in the groundwater concentrations of gasoline constituents over the period of 2001 to 2011 (85% decrease for benzene, 96% for MTBE, and 87% for TBA), measured as the change in the median of the maximum site concentrations over time. In addition, records of the sites for which continuous monitoring records were available for the full 10-year period (benzene: 1128 sites; MTBE: 1109 sites, TBA: 816 sites) showed benzene and MTBE levels to decrease continuously over this time period, while the maximum concentrations of TBA increased moderately over the period of 2001 to 2004 and then decreased from 2005 to 2011. The study found that the temporary build-up and subsequent decrease of TBA concentrations could be closely matched by a sequential first-order degradation model, which accounted for the generation of TBA as a product of MTBE degradation, followed by the biodegradation of the TBA itself (McHugh et al. 2013).

Conclusions

In this paper, we have combined the results of 13 previously published studies that surveyed the length and stability condition of affected groundwater plumes associated with releases of gasoline fuels from USTs at numerous service station facilities. These studies combined have addressed over 500 plumes for MTBE, over 1300 plumes for benzene, and 108 plumes for TBA, plus evaluation of concentration trends of all three gasoline constituents over a 10-year period for over 4000 UST sites in California. Employing a variety of approaches, these studies arrive at similar findings with regard to plume length and stability, which suggests that, in combination, these data and the related statistical parameters presented in this review paper provide a reliable characterization of benzene, MTBA, and TBA plume behavior at the majority of UST sites across the United States. Key findings regarding the statistical distribution of plume lengths and plume stability conditions at UST sites include the following:

1. *Comparison of MTBE and Benzene Plumes.* The plume delineation studies show MTBE and benzene plumes to be of comparable length at most sites. For example, at a 10 µg/L delineation limit, the 90th percentile MTBE and benzene plume lengths are 400 feet (336 sites) and 345 feet (772 sites), respectively, a relative difference of 16%. Similarly, at a 5 µg/L delineation limit, the 90th percentile MTBE and benzene plume lengths are

530 feet (96 sites) and 425 feet (165 sites), respectively, a relative difference of 25%, although these values should be considered tentative due to smaller numbers of wells and only one study for MTBE. The vast majority of wells for both MTBE (91%) and benzene (92%) exhibit nonincreasing concentrations over time (i.e., stable, no trend, decreasing, or exhausted), and plume lengths also are predominantly nonincreasing over time for MTBE (93%) and benzene (94%). Consequently, reported plume lengths for benzene and MTBE are likely indicative of their maximum future lengths, as the plumes are generally not increasing in size and concentration.

2. *TBA Plumes Compared to MTBE and Benzene Plumes.* TBA plumes have been found to be of comparable length to benzene and MTBE plumes, with the majority of TBA plumes also nonexpanding (68%), although at a lower percentage than observed for MTBE or benzene plumes (Kamath et al. 2012). At over 4000 sites evaluated, TBA concentration trends over time showed an initial increase, followed by a decreasing concentration at rates comparable to those observed for MTBE and benzene (McHugh et al. 2013).
3. *Consistency Among Various Studies:* The various plume studies, conducted in different geographic regions and in a variety of hydrogeologic regimes, have found plume length statistics to fall into a relatively narrow range, suggesting that hydrogeologic conditions may be less important than other factors (such as the spill volume and biodegradation effects) in defining plume behavior, as has been observed in these and other studies (Reid et al. 1999; Mace et al. 1997; Newell and Connor 1998; Shorr and Rifai 2002; Wilson 2003). Rather, the similar biodegradation characteristics of MTBE and benzene, both of which are degradable in aerobic and most anaerobic geochemical settings, may be responsible for the comparable dimensions and stability conditions of these plumes.

Supporting Information

Additional Supporting Information may be found in the online version of this article:

Appendix S1. Review of Quantitative Surveys of the Length and Stability of MTBE, TBA, and Benzene Plumes in Groundwater at UST Sites.

Table S1. Statistical plume length data from the literature for MTBE, benzene, and TBA

Table S2. Plume stability results for MTBE, benzene, and TBA

Table S3. Concentration trend results for MTBE, benzene, and TBA

Table S4. Results from Stevens et al. (2006) analysis

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