SUMMARY

The purpose of this evaluation is to characterize concentrations and attenuation rates for BTEX, MTBE, and tert-butyl alcohol (TBA) in groundwater at gasoline release sites in California based on analysis of the California GeoTracker database. California began to phase out the use of MTBE as an oxygenate in gasoline in 2000 and the use was eliminated entirely starting January 1, 2004. As a result, decreases in MTBE concentrations in groundwater reflect progress in the remediation (including natural attenuation) of pre-2004 releases. Because benzene and other hydrocarbons remain in gasoline, decreases in dissolved phase concentrations of these constituents in groundwater reflect both progress in remediation of past releases and success in the prevention of new releases.

The GeoTracker database is maintained by the California State Water Board and is the data management system for sites with impacts to groundwater. The GeoTracker database contains groundwater monitoring results for 12,714 corrective action sites, including 10,760 Leaking Underground Fuel Tank (LUFT) sites. For these sites, groundwater monitoring results are generally available in electronic database form for the time period 2001 to present, although recent monitoring results may not appear in the database until a few months after they are collected.

Because of the large number of sites included in the GeoTracker database, this database can be used to gain insights into the recent progress of groundwater cleanup at LUFT sites in California. A review of the database indicates that, on average, concentrations of gasoline constituents in groundwater have decreased significantly since 2001. Key points in this regard include:

Decrease in Constituent Concentrations: Maximum site concentrations of gasoline constituents, on average, have decreased significantly from 2001 to 2011. The 2010-2011 maximum site benzene concentrations have decreased by an average of 85% compared to the post 2001 historical maximum, and maximum site MTBE concentrations have decreased by an average of 96%. On average, maximum site concentrations of TBA showed a modest increase over the time period of 2001 to 2005, but have decreased since 2005. In 2010-2011, the average decrease in TBA concentration was 89% compared to the post 2001 historical site maximum concentration. Evaluation of the MTBE and TBA monitoring data using a sequential degradation model suggests that the observed lag in TBA attenuation is attributable to the generation of TBA through the biodegradation of MTBE. This TBA trend is consistent with what would be expected based on known MTBE and TBA sources and attenuation processes including the generation of TBA through biodegradation of MTBE and subsequent biodegradation of TBA (Hyman, 2012).
Prior studies evaluating gasoline constituent dissolved plume behavior at gasoline release sites have found that these plumes most commonly stabilize in length within a few years of a gasoline release and eventually shrink back towards the source. Specifically, monitoring data for groundwater plumes at over 400 gasoline release sites in multiple states (Kamath et al., 2011), 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 benzene and MTBE plumes typically tend to stabilize at relatively short lengths (i.e., 90% less than 540 ft).

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 75% of MTBE plumes evaluated at those times were already stable or decreasing in length. In the 2011 study (Kamath et al., 2011), 95% of benzene plumes, 90% of MTBE plumes, and 68% of TBA plumes were stable or shrinking. At the majority of sites studied, the highest concentrations of gasoline constituents were found in the source area throughout the life-cycle of the plume. The results from these prior studies in combination with this study suggest that the observed decreases in constituent concentrations at California LUFT sites since 2001 are attributable to destructive attenuation processes rather than migration of dissolved constituents away from the source zone (i.e., detached plumes).

**Attenuation Rates and Site Risks:** Using data from the GeoTracker database, source zone attenuation rates were calculated based on the observed change in concentrations of gasoline constituents over time at individual sites. These attenuation rates reflect the effects of both natural attenuation and active remediation on the concentration of gasoline constituents in source area groundwater at these sites. The median first-order attenuation rates for benzene and MTBE were 0.18 yr\(^{-1}\) and 0.36 yr\(^{-1}\), respectively, corresponding to half-lives of 3.9 and 1.9 years. A sequential degradation model (considering biodegradation of MTBE with generation of TBA and biodegradation of TBA) applied to monitoring data from a large set of sites suggests an attenuation rate for TBA of 0.2 yr\(^{-1}\), corresponding to a half-life of 3.5 years.

The significant decrease in dissolved concentrations of gasoline constituents in groundwater since 2001 indicates that the potential risk associated with exposure to affected groundwater has also decreased significantly. Based on the observed attenuation rates, concentrations are expected to continue to decrease significantly over time. As a result of this continual decrease in concentration, the risk associated with potential long-term exposure to affected groundwater is significantly less than implied by current concentrations of benzene, MTBE, and other gasoline constituents.
ANALYSIS OF GEOTRACKER DATABASE

The GeoTracker database was downloaded from the web site maintained by the California State Water Board on October 17, 2011. This database contained groundwater monitoring data in electronic form for 12,714 sites, covering the time period of January 2000 to October 2011. Because the monitoring results appeared to be most comprehensive for the time period of July 2001 to June 2011, this 10-year time period was the focus of our analysis.

Concentrations of Gasoline Constituents in Groundwater.

In order to evaluate overall progress in site remediation in California, the maximum site concentrations of gasoline constituents were evaluated for the available time period. For each site, the maximum site concentration for each gasoline constituent was taken as the maximum reported concentration for any monitoring well for each six month time period over the evaluation time (i.e., July 2001 to December 2001, January 2002 to June 2002, etc.). For each time period, the median of these maximum concentrations was taken as a representative maximum concentration for sites across California and the change in this median value over time was used to evaluate progress in remediation. The results of this analysis are presented in Figures 1 to 4.

BTEX Concentrations: Figure 1 shows the median of the maximum concentrations across all sites over time for benzene, ethylbenzene, toluene, and xylenes. This analysis included all sites where the constituent was detected in at least one sample during the 10-year evaluation period. Each six-month time period includes all of the sites where the constituent was analyzed in at least one sample during that six-month period even if the maximum concentration for that six-month period was non-detect. The number of sites monitored increased from 2001 to 2008 and then decreased from 2008 to 2011. The apparent stabilization in maximum BTEX concentrations from 2008 to 2011 based on the analysis of all sites with monitoring data is most likely due to closure of clean sites, resulting in sites with the lowest constituent concentrations dropping from the analysis of monitoring data from the most recent years.

Figure 2 shows the median of maximum concentrations across all sites over time for the subset of sites with monitoring results available for the entire time period of 2001 to 2011 (indicating an absence of regulatory closure). For this set of sites, the maximum site concentrations decrease continuously, providing additional evidence that the apparent stabilization observed in the full dataset is due to closure of clean sites.

MTBE and TBA Concentrations: Figures 3 and 4 are equivalent to Figures 1 and 2, but for MTBE and TBA. MTBE concentrations in groundwater have dropped rapidly since 2001. TBA concentrations have also decreased, but with an apparent lag.

For the subset of sites with monitoring results available for the entire time period of 2001 to 2011 (Figure 4), median maximum site TBA concentrations increase from 2001 to 2005 and then decrease after 2005.

Magnitude of Concentration Decrease: Figures 5 and 6 summarize the range of concentration decreases observed across open LUFT sites in California that were open in 2011. Figure 5 show the range of historical maximum concentrations for the time
period of 2001 to 2011 for MTBE, TBA, and benzene and the range of the current maximum concentrations (2010 to 2011) for the same three constituents. Figure 6 shows the range of reduction in maximum site concentrations of MTBE, TBA, and benzene expressed in orders of magnitude. This analysis shows that the average concentration reduction has been 96% for MTBE, 89% for TBA, and 85% for benzene.

**Source Attenuation Rates for Benzene and MTBE.**

In order to characterize source zone attenuation rates for the sites in the GeoTracker database, $k_{\text{point}}$ values were estimated using regression analysis. Source zone attenuation rates were calculated for each site with at least five years of monitoring data for the constituent of interest (benzene or MTBE). The best-fit attenuation rates were determined for the decrease in maximum site concentration over time using least squares regression for first-order attenuation:

$$C = C_0 e^{-k_{\text{point}} t}$$

Where:

- $C$ = The representative (i.e., maximum) COC concentration for the six-month monitoring period (ug/L)
- $t$ = Time (years)
- $k_{\text{point}}$ = Source attenuation rate (determined using regression analysis, yr$^{-1}$)
- $C_0$ = Initial concentration (determined using regression analysis, ug/L). Note that the value for $C_0$ was determined for an arbitrary “zero” time and the resulting values were not used for any subsequent analysis.

Because this analysis is based on the overall change in maximum concentration over time at each site, the resulting attenuation rates reflect the combined effects of all attenuation processes that are occurring at each site (e.g., biodegradation, dispersion, dissolution from residual NAPL, physical removal from active remedies, etc.).

The results of this analysis are summarized in Table 1.

**Table 1. First-Order Source Attenuation Rates**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Number of Sites</th>
<th>Median $k_{\text{point}}$ (yr$^{-1}$)</th>
<th>Median Half Life (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>4765</td>
<td>0.18</td>
<td>3.9</td>
</tr>
<tr>
<td>MTBE</td>
<td>4284</td>
<td>0.36</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Notes: 1) Number of sites with five or more years of monitoring data for the constituent.

The evaluation of source attenuation rates is consistent with the observed decrease in maximum concentrations of gasoline constituents over time indicated by the analyses shown in Figures 1 to 6. Attenuation rates for TBA were not included because the concentration of TBA in groundwater is a function of TBA generation as a result of biodegradation of MTBE in addition to TBA attenuation processes.

**Effect of Site Remediation Technology of Source Attenuation Rates.**

The GeoTracker database provides information concerning the types of technologies used at remediation sites in California; however, the database does not provide information on when these technologies were implemented or how long they were
operated. For sites with sufficient data to evaluate source attenuation rates, we evaluated the types of remediation technologies applied (see Figure 7).

In order to evaluate the effect of site remediation on source attenuation, source attenuation rates were sorted by the remediation technology applied (Table 2). Little difference in source attenuation rates were observed between sites based on the type of remediation technology applied. This analysis suggests that the type of remediation technology applied has, at most, a relatively small effect on source attenuation rates and that NAPL depletion (dissolution) contributes most significantly to declining concentrations.

A larger difference in attenuation rates was observed for benzene between sites with and without Free Product Recovery identified as a remediation technology. The median benzene attenuation rate was 45% slower at sites where NAPL Recovery was identified as a remediation technology. Because Free Product Recovery is more likely to be implemented at sites with larger release volumes, this suggests that benzene source attenuation rates are slower at sites with larger release volumes (i.e., greater NAPL volume resulting in slower source depletion).

### Table 2. Effect of Site Remediation Technology on Source Attenuation Rates

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Number of Sites</th>
<th>$K_{Point}$ (yr$^{-1}$)</th>
<th>Median Half Life (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All sites with sufficient data for calculation of attenuation rates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>4765</td>
<td>0.18</td>
<td>3.9</td>
</tr>
<tr>
<td>MTBE</td>
<td>4284</td>
<td>0.36</td>
<td>1.9</td>
</tr>
<tr>
<td>All sites with information on type of site remediation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2777</td>
<td>0.21</td>
<td>3.3</td>
</tr>
<tr>
<td>MTBE</td>
<td>3194</td>
<td>0.38</td>
<td>1.8</td>
</tr>
<tr>
<td>Sites with Soil Excavation or MNA identified as the only remediation technology</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>371</td>
<td>0.19</td>
<td>3.7</td>
</tr>
<tr>
<td>MTBE</td>
<td>492</td>
<td>0.32</td>
<td>2.2</td>
</tr>
<tr>
<td>Sites with Soil Vapor Extraction identified as the only remediation technology</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>267</td>
<td>0.23</td>
<td>3.0</td>
</tr>
<tr>
<td>MTBE</td>
<td>298</td>
<td>0.39</td>
<td>1.8</td>
</tr>
<tr>
<td>Sites with GW Pump and Treat identified as the only remediation technology</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>93</td>
<td>0.18</td>
<td>3.9</td>
</tr>
<tr>
<td>MTBE</td>
<td>134</td>
<td>0.47</td>
<td>1.5</td>
</tr>
<tr>
<td>All sites with Free Product Recovery identified as a remediation technology</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>553</td>
<td>0.13</td>
<td>5.4</td>
</tr>
<tr>
<td>MTBE</td>
<td>574</td>
<td>0.31</td>
<td>2.3</td>
</tr>
<tr>
<td>All sites without Free Product Recovery identified as a remediation technology</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>2224</td>
<td>0.24</td>
<td>2.9</td>
</tr>
<tr>
<td>MTBE</td>
<td>2620</td>
<td>0.39</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Note: 1) Analysis only includes sites with one or more remediation technologies identified in the GeoTracker database as being applied at the site. Sites with no information concerning the type of remediation were not included. 2) Sites with soil excavation only, sites with MNA only, and sites with soil excavation and MNA were combined into a single group because the benzene and MTBE attenuation rates for these three separate groups varied by less than 10%. In addition, soil excavation typically involves removal of soil from the vadose zone rather than below the water table.
Evaluation of TBA Generation and Attenuation.

Biodegradation of MTBE at LUFT sites can yield TBA as a degradation product (USEPA, 2005; Hyman 2012). As a result, the TBA concentration in groundwater is a function of both TBA generation rates (from MTBE degradation) and TBA degradation rates. For the set of sites with continuous monitoring data from 2001 to 2011, the link between MTBE and TBA concentrations was evaluated using a sequential degradation model that accounts for both the generation and degradation of TBA (Carr et al., 2000):

\[
C_{TBA} = \frac{MW_{TBA}}{MW_{MTBE}} \frac{k_{MTBE}}{k_{MTBE}} C_{0,MTBE} \left[ \exp( -k_{MTBE} t ) \right] \exp( -k_{TBA} t )
\]

Where:

\[
\begin{align*}
C_{TBA} & = \text{TBA Concentration (ug/L)} \\
MW_{TBA} & = \text{Molecular weight of TBA (C}_4H_{10}O; 74 \text{ g/mol}) \\
MW_{MTBE} & = \text{Molecular weight of MTBE (C}_5H_{12}O; 88 \text{ g/mol}) \\
k_{TBA} & = \text{First-order attenuation rate for TBA (0.20 yr}^{-1} \text{)} \\
k_{MTBE} & = \text{First-order attenuation rate for MTBE (0.39 yr}^{-1} \text{)} \\
C_{0,MTBE} & = \text{Initial MTBE concentration (5400 ug/L in July 2000)} \\
t & = \text{Time since July 2000 (yr)}
\end{align*}
\]

The MTBE attenuation rate (0.39 yr\(^{-1}\)) was based on the best-fit attenuation rate for the MTBE concentration data for this set of sites. The initial MTBE concentration and starting time were set to yield an MTBE concentration in January 2002 of 3000 ug/L and a TBA concentration in January 2002 of 1700 ug/L, consistent with the observed concentrations in January 2002. The TBA attenuation rate was determined iteratively to obtain a good visual fit to the observed change in TBA concentration over time from 2002 to 2011. The final model-predicted TBA concentration is shown as the solid purple line on Figure 4. The model result is consistent with biodegradation of MTBE as the primary source of TBA in groundwater. The result suggests that net attenuation of TBA should continue to increase since the continued decrease in MTBE concentration corresponds with a continued decrease in TBA generation.

The resulting TBA source attenuation rate was 0.20 yr\(^{-1}\), corresponding to a TBA source half life of 3.5 years. This is consistent with the average 89% decrease in the current maximum TBA concentration compared to the historical maximum TBA concentration for the sites in the GeoTracker database. A recent study of TBA plume behavior at LUFT sites found that 68% of TBA plumes were stable or shrinking in lateral extent and only 6% were detached from the original source (Kamath et al., 2011). This indicates that the primary source attenuation mechanism for TBA is destructive rather than advective transport away from the source.

ACKNOWLEDGEMENTS

This work has been funded, in part, by the American Petroleum Institute (API). We thank members of the API Soil and Groundwater Technical Group for helpful review and comments.

REFERENCES


FIGURE 1. DECREASE IN MAXIMUM SITE CONCENTRATION OF BTEX: ALL SITES WITH ANY MONITORING DATA FROM 2001 TO 2011

Note: Charts show median of maximum concentrations for all sites vs. time for UST sites in California with any monitoring data available between 2001 and 2011.

KEY POINTS:
1. BTEX CONCENTRATIONS IN GROUNDWATER AT UST SITES IN CALIFORNIA HAVE DECREASED SIGNIFICANTLY OVER THE PAST 10 YEARS.
2. THE NUMBER OF SITES MONITORED HAS DECREASED SINCE 2008, MOST LIKELY REFLECTING CLOSURE OF CLEAN SITES.
3. THE APPARENT STABILIZATION OF MAXIMUM SITE CONCENTRATIONS SINCE 2008 MOST LIKELY REFLECTS SITES DROPPING OUT OF THE DATASET DUE TO REGULATORY CLOSURE.
FIGURE 2. DECREASE IN MAXIMUM SITE CONCENTRATION OF BTEX: SITES OPEN FROM 2001 THROUGH 2011

Note: Charts show median of maximum concentration for all sites vs. time for UST sites in California with monitoring data available for the full time period 2001 to 2011 (Benzene – 1128 sites, ethylbenzene – 1123 sites, toluene – 1130 sites, xylenes – 723 sites).

KEY POINT: BTEX CONCENTRATIONS IN GROUNDWATER AT UST SITES THAT HAVE NOT RECEIVED REGULATORY CLOSURE HAVE DECREASED CONTINUOUSLY OVER THE PAST 10 YEARS.
FIGURE 3. DECREASE IN MAXIMUM SITE CONCENTRATIONS OF MTBE AND TBA: ALL SITES WITH ANY MONITORING DATA FROM 2001 TO 2011

KEY POINTS:
1. MTBE CONCENTRATIONS IN GROUNDWATER AT UST SITES IN CALIFORNIA HAVE DECREASED SIGNIFICANTLY OVER THE PAST 10 YEARS.
2. MEDIAN MAXIMUM SITE TBA CONCENTRATIONS HAVE CHANGED LESS OVER THE TIME PERIOD.
3. THE NUMBER OF SITES MONITORED HAS DECREASED SINCE 2008, MOST LIKELY REFLECTING CLOSURE OF CLEAN SITES.
4. THE CONCENTRATION TRENDS SINCE 2008 ARE LIKELY AFFECTED BY THE CLEANEST SITES DROPPING OUT OF THE DATASET DUE TO REGULATORY CLOSURE.
FIGURE 4. DECREASE IN MAXIMUM SITE CONCENTRATIONS OF MTBE AND TBA: SITES OPEN FROM 2001 THROUGH 2011

Note: Charts show median of maximum site concentration vs. time for UST sites in California with monitoring data available for the full time period 2001 to 2011 (MTBE – 1109 sites, TBA – 816 sites).

On TBA Chart, the purple line is the model-predicted TBA concentration using a sequential decay model that accounts for the generation of TBA from the biodegradation of MTBE. The model uses an MTBE half life of 1.8 yrs and a TBA half life of 3.5 yrs and was initialized with starting concentration of 3000 ug/L MTBE and 1700 ug/L TBA on January 1, 2002.

KEY POINTS:
1) MTBE CONCENTRATIONS IN GROUNDWATER AT UST SITES THAT HAVE NOT RECEIVED REGULATORY CLOSURE HAVE DECREASED CONTINUOUSLY OVER THE PAST 10 YEARS.
2) THE APPARENT LAG IN TBA ATTENUATION IS LIKELY DUE TO TBA GENERATION RESULTING FROM MTBE DEGRADATION.
3) BIODEGRADATION APPEARS TO BE AN IMPORTANT MECHANISM FOR MTBE ATTENUATION.
Notes: 1) Sites are designated as "open sites" if the GeoTracker contains results of MTBE and/or TBA testing from at least 2 sampling events conducted after January 2010. 2) Only sites with a minimum of 3 groundwater monitoring wells and with at least 4 years of groundwater testing for MTBE or TBA are included in this evaluation. Sites where both MTBE and TBA have never been detected are not included in this evaluation. 3) For this evaluation, if the current or historical maximum MTBE or TBA concentration was reported as a non-detect, then a proxy concentration of 1 µg/L was used.

**KEY POINT:** AT OPEN LUFT SITES, CURRENT (post-2010) MAXIMUM CONCENTRATIONS OF BENZENE, MTBE, AND TBA ARE SIGNIFICANTLY LOWER THAN HISTORICAL (post-2001) MAXIMUM CONCENTRATIONS.
FIGURE 6. REDUCTION IN MAXIMUM CONCENTRATION AT OPEN LUFT SITES IN CALIFORNIA (EXPRESSED IN ORDERS OF MAGNITUDE REDUCTION)

Notes: 1) Sites are designated as “open sites” if the GeoTracker contains results of MTBE and/or TBA testing from at least 2 sampling events conducted after January 2010. 2) Only sites with a minimum of 3 groundwater monitoring wells and with at least 4 years of groundwater testing for MTBE or TBA are included in this evaluation. Sites where both MTBE and TBA have never been detected are not included in this evaluation. 3) The MTBE whisker does not include 90 sites that had detectable concentrations of TBA but not MTBE during the entire monitoring history (total 4226 – 90 = 4176 sites). 4) The TBA whisker does not include 339 sites that had detectable concentrations of TBA but not MTBE during the entire monitoring history (total 4118 – 339 = 3779 sites). 5) For this evaluation, if the current or historical maximum MTBE or TBA concentration was reported as a non-detect, then a proxy concentration of 1 µg/L was used.

KEY POINT: AT OPEN LUFT SITES, MTBE CONCENTRATIONS HAVE DECREASED BY AN AVERAGE OF 96%, TBA CONCENTRATIONS HAVE DECREASED BY AN AVERAGE OF 89%, AND BENZENE CONCENTRATIONS HAVE DECREASED BY AN AVERAGE OF 85%.
FIGURE 7. TECHNOLOGIES APPLIED AT REMEDIATION SITES IN CALIFORNIA

**KEY POINT**: SOIL EXCAVATION, SOIL VAPOR EXTRACTION AND GROUNDWATER PUMP AND TREAT ARE THE THREE MOST COMMONLY USED TECHNOLOGIES AT REMEDIATION SITES IN CALIFORNIA

Note: Chart shows remediation technologies applied at 3194 remediation sites in the GeoTracker database. The total percentage is greater than 100%, as more than one technology was applied at some sites.