



Lawrence Livermore National Laboratory
University of California
Livermore, California 94551

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An Evaluation of MTBE Impacts to California Groundwater Resources

Authors

Anne M. Happel
Edwin H. Beckenbach*
Rolf U. Halden

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*University of California, Berkeley



Environmental Protection Department
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EXECUTIVE SUMMARY

Methyl *tertiary*-butyl ether (MTBE) is a fuel oxygenate added to gasoline to reduce air pollution and increase octane ratings. Widespread use of this chemical has resulted in frequent detections of MTBE in samples of shallow groundwater from urban areas throughout the United States (Squillace *et al.*, 1996). Limited contamination of drinking water has also occurred and is of concern because MTBE is considered a possible human carcinogen by the U.S. Environmental Protection Agency (US EPA) and has a disagreeable taste and odor at extremely low concentrations. Our work focuses on the inadvertent release of this compound to the environment from leaking underground fuel tanks (LUFTs) with the goal of providing information on the potential for MTBE to impact California's groundwater resources.

Because data collected for regulatory compliance from any one LUFT site are limited, recent studies evaluating the behavior of fuel hydrocarbon releases from a population perspective have proved valuable in evaluating contaminant behavior (Rice *et al.*, 1995; Mace *et al.*, 1997; Dooher, 1998). Therefore, we have focused our efforts on analysis of data from populations of LUFT sites to elucidate general trends in the behavior of MTBE. Monitoring for this compound at California sites has been required only since July 1996. As a result, sufficient MTBE data for even the simplest statistical and time-series analyses are just now becoming available. Results presented here are the initial findings of an ongoing study.

The initial objectives of our analysis were to answer several key questions:

Are US EPA and ASTM Methods applicable for the analysis of MTBE and similar fuel oxygenates in groundwater samples from LUFT sites?

We have tested analytical methods to determine the precision and accuracy of oxygenate analysis in groundwater containing dissolved gasoline compounds. EPA Method 8020A/21B is most commonly used for analysis of MTBE in groundwater from LUFT sites; we identified the following limitations. First, analysis of *tertiary*-butyl alcohol (TBA) suffered from poor sensitivity and yielded unreliable results even when only small amounts of gasoline were present in the sample ($> 500 \mu\text{g L}^{-1}$). Second, in the presence of high concentrations of non-oxygenated gasoline ($50,000 \mu\text{g L}^{-1}$), EPA Method 8020A/21B yielded false-positive results for all oxygenates tested including MTBE, TBA, diisopropyl ether (DIPE), ethyl *tertiary*-butyl ether (ETBE), and *tertiary*-amyl methyl ether (TAME). These misidentifications resulted from using method detection limits (MDLs) determined in clean water rather than up to two orders of magnitude higher values appropriate for the analysis of oxygenates in samples with high total petroleum hydrocarbon-gasoline (TPH-g) content. EPA Method 8020A/21B should be revised to account for this phenomenon of variable analyte sensitivity due to matrix effects thereby minimizing the occurrence of false-positive misidentification of oxygenates in the future. In contrast, EPA Method 8260A and a modified version of ASTM Method D4815 produced excellent results for all analytes regardless of the amount of gasoline interferences present in the sample.

Overall, EPA Method 8020A/21B was identified as a very conservative monitoring tool due to the lack of false-negative results, and its tendency for over-estimation of analyte concentrations and false-positive misidentifications. However, in the absence of required method modifications, more definitive tests such as EPA Method 8260A and the modified ASTM Method D4815 are recommended when monitoring low concentrations of oxygenates in samples that may have high regulatory impact.

How frequently is MTBE detected in groundwater at gasoline release sites?

We examined groundwater data from 236 LUFT sites located in 24 counties within California that contained a total of 1,858 monitoring wells. In 1995/96, MTBE detections were reported at 78% of these sites, indicating that this oxygenate is a likely contaminant at the majority of LUFT sites in California where fuel hydrocarbons have impacted groundwater. Maximum concentrations found at these sites ranged from several $\mu\text{g L}^{-1}$ to approximately 100,000 $\mu\text{g L}^{-1}$, indicating a wide range in the magnitude of potential MTBE impacts at gasoline release sites.

What is the overall frequency of monitoring and occurrence of MTBE in California's public drinking water wells?

As of March 1998, 32% of the 6,593 active drinking water wells within large public water supply systems and up to 7% of wells in small water systems have been monitored for MTBE as reported to the California Department of Health Services. Among the 2,297 active public water supply wells monitored, the frequencies of impact by MTBE (0.35 percent) and benzene (0.42 percent) were similar given current action levels of 20 $\mu\text{g L}^{-1}$ and 1 $\mu\text{g L}^{-1}$, respectively. For MTBE, this frequency of impact to public drinking wells may not be a reliable indicator of future trends because it reflects a history of releases, including those involving gasoline formulations containing no or only low volumes of MTBE. In addition, it is important to note that, even infrequent occurrences of MTBE may have significant effects on regional water supplies as illustrated by the closure of the City of Santa Monica's groundwater wells.

How do the spatial extents of MTBE and benzene plumes at gasoline release sites compare?

We have used 1995/96 data from 63 California LUFT sites to define concentration contours of dissolved MTBE and benzene plumes using action levels of 20 and 1 $\mu\text{g L}^{-1}$, respectively. Among these plume study sites, data from existing monitoring well networks were sufficient to estimate the length of 50 MTBE and benzene plumes. Cumulative distributions of plume lengths revealed that, on a population-wide basis, MTBE plumes were typically equivalent in length, or shorter than benzene plumes. On a site-by-site basis, this was also true in approximately 81% of the cases. Further at an individual LUFT site, the length of a benzene plume was only moderately correlated with the length of the corresponding MTBE plume; thus the length of a benzene plume cannot be used to predict the extent of MTBE impact.

For the majority of LUFT sites analyzed in this study, our results suggest that dissolved benzene plumes were of larger regulatory concern during 1995/96 than the respective MTBE plumes.

Given both the anticipated high mobility and high recalcitrance of MTBE in the subsurface, these results appear to contradict expected behavior. However, it is important to realize that, for the majority of LUFT sites, release histories for MTBE and benzene most likely differed significantly; recent releases of gasoline containing significant quantities of MTBE may have occurred at sites with a long history of contamination with less or non-oxygenated fuels. Whereas several previous studies show that the vast majority of benzene plumes are apparently stable, the present limited analysis of time-series data suggests that MTBE may behave differently resulting in a gradual spatial dissociation of MTBE and BTEX plumes over time. Thus, plume lengths measured at a single point in time, *e.g.*, 1995/96, cannot be indicative of future MTBE plume behavior and its relationship to that of benzene. In addition, comparison of risk-based plume contours are inherently dependent on accepted regulatory action levels. In the near future, California may set these action levels below the 20 $\mu\text{g L}^{-1}$ level used for comparison in this study.

How do MTBE groundwater plumes behave over time?

We have analyzed data from 29 sites located in San Diego County where MTBE monitoring data extend from the beginning of 1992 through the end of 1996. This dataset consisted of 2,320 samples collected at 327 monitoring wells which had been analyzed simultaneously for MTBE, total gasoline petroleum hydrocarbons (TPH), as well as benzene, toluene, ethylbenzene, and xylenes (BTEX). Overall, our analysis of MTBE and hydrocarbon contamination at these sites provides suggestive and compelling evidence to the following:

- The probability of co-occurrence of MTBE and BTEX compounds detected in individual monitoring wells decreased significantly over time (from approximately 80% to 60% over a period of 3 years), whereas the overall frequency of detection of these compounds remained consistent. Assuming that the majority of hydrocarbon plumes are stable, the observed gradual dissociation of BTEX and MTBE plumes indicates that MTBE plumes are mobile.
- MTBE concentrations in the downgradient wells of the San Diego County sites were often equivalent to or significantly higher than corresponding concentrations of BTEX compounds, implying that at many of these sites MTBE was leaving established monitoring networks at significantly higher concentrations than individual BTEX fuel components. The relevance of this implication is dependent upon accepted action levels for MTBE as well as its potential for *in situ* degradation. Using current regulatory levels of 20 and 1 $\mu\text{g L}^{-1}$ for MTBE and benzene, respectively, the action level ratio of 20 to 1 was exceeded in approximately 30% of the downgradient wells at the San Diego County sites suggesting that MTBE impacts were more significant than those of benzene at a minority of these LUFT sites. However, when extrapolating to the future, this assessment is likely optimistic, since both the high potential for *in situ* biodegradation of benzene and retardation of benzene relative to MTBE are expected to result in attenuation of benzene plumes to regulatory action levels within a shorter distance than MTBE.

- Variability in hydrologic parameters, such as high precipitation events, resulted in brief increases in MTBE concentrations in monitoring wells with low TPH-g impacts ($< 1000 \mu\text{g L}^{-1}$). Spikes in MTBE concentrations were observed after the particularly wet winters of 1992/93 and 1994/95. These concentration surges are of particular concern because they suggest that periodic monitoring over limited time intervals may fail to detect the departure of significant amounts of oxygenate from the monitoring network. This may be especially important when evaluating the stability of an individual plume or when estimating mass migrating beyond downgradient monitoring wells.
- Reductions of benzene concentrations by as much as several orders of magnitude in the downgradient direction were observed within existing monitoring networks indicating significant attenuation of benzene at the majority of LUFT sites. By comparison, attenuation of MTBE appeared to be much more limited because concentration reductions generally did not exceed one order of magnitude. These results are consistent with the hypothesis that MTBE is generally recalcitrant and not likely to undergo the rapid attenuation seen for the more biodegradable BTEX compounds.

In summary, the following conclusions are supported by our results:

1. MTBE is a frequent and widespread contaminant in shallow groundwater throughout California. There are presently 32,409 LUFT sites recognized in the state, 13,278 at which hydrocarbons are known to have impacted groundwater. A minimum estimate of the number of MTBE-impacted sites in California is greater than 10,000.
2. MTBE plumes are more mobile than BTEX plumes. Although our results using 1995/96 data indicate that, at the majority of sites, individual MTBE plumes were nearly equivalent or shorter than their corresponding benzene plumes (defined by action levels of 20 and $1 \mu\text{g L}^{-1}$ respectively), our results predict that at a portion of these sites this relationship will change over time as the contaminant plumes gradually dissociate.
3. The primary attenuation mechanism for MTBE is dispersion. Observed attenuation of BTEX and MTBE compounds at downgradient monitor wells suggests that MTBE is not significantly degrading in existing monitoring networks. Thus, MTBE may be regarded as recalcitrant under site-specific conditions. MTBE concentrations leaving these networks were greater than those of BTEX compounds at a significant portion of LUFT sites. Assuming resistance of MTBE to biodegradation, these plumes will eventually attenuate to regulatory concentration goals due to dispersion, although in contrast to BTEX compounds, the mass would not be depleted and significantly longer distances and time frames would be required.
4. MTBE has the potential to impact regional groundwater resources and may present a cumulative contamination hazard. To date, impacts of MTBE to public water systems have been limited and were similar in frequency to those of benzene. Based on historical

data, future impacts of aromatic hydrocarbons, such as benzene, to water supplies is not expected to be common, due to retardation and relative ease of biodegradation. In contrast, MTBE contamination may be a progressive problem due to the chemical's apparent recalcitrance and mobility. With a compound that appears both ubiquitous and recalcitrant, water resource management on the regional scale will become increasingly relevant. For example, the potential long-term accumulation of mass resulting from dispersion of MTBE plumes may be a key consideration for management of specific regional groundwater basins. Therefore, leak prevention is a critical requirement for the continued use of MTBE to ensure future protection of drinking water resources.

5. We have identified two major areas of uncertainty in our results. First, presently available MTBE data are limited. Second, the issue of recalcitrance of MTBE has not been resolved. Ideally, time-series data from hundreds of LUFT sites representing all hydrogeologic regions of California should be utilized to characterize the behavior and impact of MTBE plumes. Analyses of an expanded dataset are important to confirm our initial findings regarding the mobility and recalcitrance of MTBE at California LUFT sites. Further time-series analyses are necessary for predicting future MTBE impacts to groundwater resources, and assessing the vulnerability of drinking water resources.

A number of laboratory-cultured microorganisms isolated from various environments can degrade MTBE, yet there is no convincing evidence to date that this destructive process occurs quickly and/or commonly in the field. While future research is warranted to address these issues, it is appropriate to manage groundwater resources with the assumption that MTBE is both mobile and recalcitrant relative to benzene, until proven otherwise.

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1. Introduction

1.1. Background

Methyl *tert*-butyl ether (MTBE) is a fuel oxygenate added to gasoline to reduce air pollution and increase octane ratings. This research focuses solely on point source releases of MTBE from leaking underground fuel tank (LUFT) sites. In comparison to other petroleum products such as benzene, MTBE behaves differently in groundwater and may require special consideration when it escapes into the environment through gasoline releases, typically from underground and aboveground storage systems, and pipelines. MTBE has been detected frequently in samples of shallow groundwater from urban areas throughout the United States (1). Given its high water solubility and expected recalcitrance in the subsurface, MTBE, in contrast to the aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes; or BTEX, collectively), has the potential to occur at higher concentrations in groundwater, travel further from leak sources, and potentially present a cumulative contamination hazard on regional scales. Therefore, its potential to impact public and private wells may be of relatively greater concern. The goal of our work is to evaluate a population of LUFT sites thereby providing information on the potential of MTBE and benzene plumes to impact California's groundwater resources.

1.2. Requirements for Oxygenates in Gasoline

The use of gasoline oxygenates has increased dramatically in order to comply with both federal and state regulations designed to improve air quality. The wintertime "Oxygenated Fuel Program" and the year-round "Reformulated Gasoline Program" were initiated by the U.S. Environmental Protection Agency (US EPA) in 1992 and 1995, respectively, to meet requirements of the 1990 Federal Clean Air Act Amendments. This legislation mandates that oxygenates be added to gasoline to reduce emissions released to the atmosphere in areas exceeding national ambient air quality standards for carbon monoxide or ozone-forming hydrocarbons (2).

In California, the Air Resources Board implemented a statewide wintertime oxygenated fuels program in 1992; however, the initially mandated federal Oxy-fuel Program oxygen content was relaxed from 2.7 percent (Federal Mandate) by weight to 1.8 to 2.2% (~11 percent by volume for MTBE) to avoid potential increases in NO_x emissions (3). In 1996, the California Air Board mandated year-round use of California Cleaner Burning Gasoline to meet requirements of the "Reformulated Gasoline Program" and California clean air goals on a state-wide basis (3).

1.3. MTBE Usage and Production

While neither Federal nor State regulations require the use of a specific oxygenate, MTBE is most commonly utilized. In 1997, its domestic production was 8.5 billion kg (4). Essentially all MTBE produced is used for fuel oxygenation. In addition to its use to meet Clean Air Act goals, MTBE has been added to conventional gasoline at 2 to 8 percent by volume to provide octane enrichment for mid- and high-octane fuels (5). Octane enhancement with MTBE began in 1979 when lead was phased out. According to the Oxygenated Fuels Association, approximately 70 percent of the gasoline sold in the United States contains MTBE. Thus, this oxygenate may be found in new or old gasoline releases in virtually all areas of the United States (5).

Nation-wide use of MTBE has rapidly increased to a consumption rate of 10.5 million gallons per day in 1997 (6). Of this quantity, approximately 4.2 million gallons per day are consumed in California (7). Thus, the daily use of MTBE in 1997 amounted to approximately 30 million kg in the US and 12 million kg in California (Figure 1.1). Currently, nearly all the gasoline consumed in California contains MTBE (8).

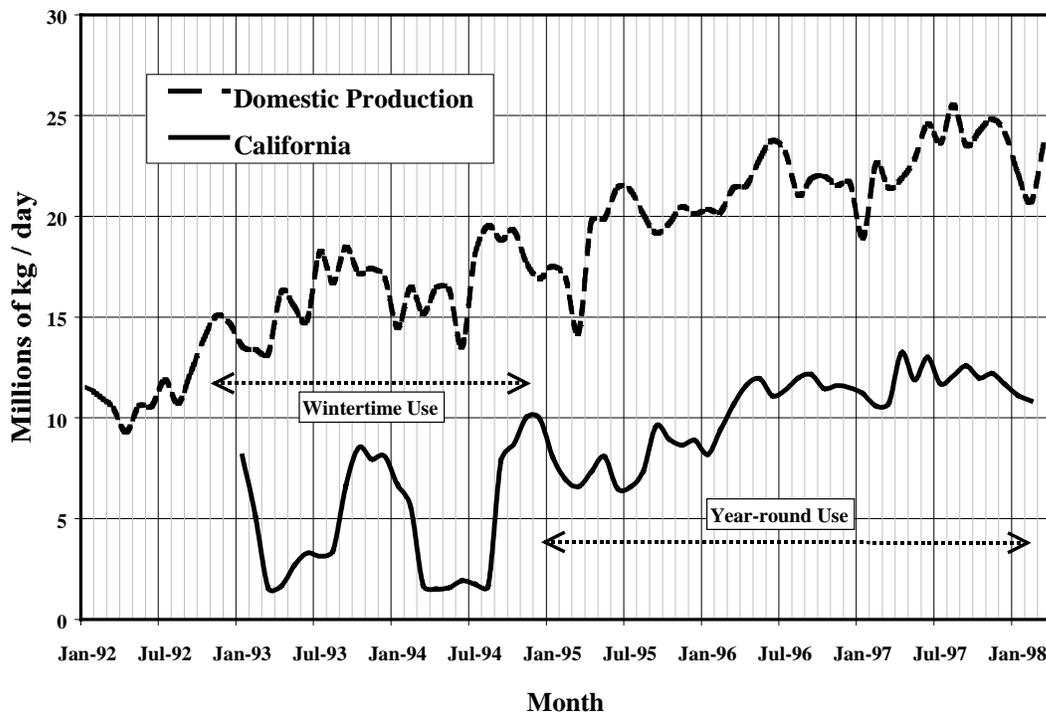


Figure 1.1. Total domestic production and California consumption in terms of total refinery inputs of MTBE. The transition from the wintertime to year-round program in California is clearly evident ($10^6 \text{ kg day}^{-1} = 2.8 \times 10^6 \text{ gallons day}^{-1}$). (Data from the Office of Oil and Gas, Energy Information Administration, U.S. Department of Energy)

1.4. Regulatory Action Levels

Drinking water standards for contaminants are set at the national level and the state level by the US EPA and the California Department of Health Services (DHS), respectively. It is the responsibility of these agencies to adopt primary and secondary maximum contaminant limits (MCLs) based on human health concerns and aesthetic concerns or technical feasibility, respectively. A contaminant may warrant regulation based either on potential health impacts, potential resource degradation or both. In the case of MTBE both concerns are appropriate since it is considered a potential carcinogen and has a disagreeable taste and odor at low concentrations.

US EPA has suggested an unenforceable health advisory for MTBE concentrations in drinking water. A draft health advisory of 20-200 $\mu\text{g L}^{-1}$ (9) based on health concerns was proposed in 1992. This was modified to an official health advisory of 20-40 $\mu\text{g L}^{-1}$ in 1997 (10) based both on health concerns and aesthetic considerations (taste and odor).

At the Federal level it is unlikely that enforceable standards will be adopted soon (11). Presently, the US EPA has designated MTBE as an unregulated chemical. The 1996 amendments to the Safe Drinking Water Act require that a list of unregulated contaminants be established (Drinking Water Contaminant Candidate List) in order to determine regulatory priorities. Compounds on this list are segregated as regulatory determination priorities, research priorities, and occurrence priorities. As of February 1998 MTBE was listed as a research priority and occurrence priority but not a regulatory determination priority. Specifically, US EPA's position is that there is a lack of information regarding health research, treatment research and occurrence data that prevents the adoption of sound standards for MTBE. Of those compounds considered regulatory priorities, five or more will be selected for potential regulation by August 2001. If regulations are considered appropriate, they must be proposed by August 2003 and enacted by February 2005. Since MTBE is not currently a regulatory priority, it does not appear likely that standards can be enacted until after February 2005. Updates to priority lists will be based on the National Drinking Water Contaminant Occurrence Database (NDOC) and the Unregulated Contaminant Monitoring Regulations, both of which are to be completed in August of 1999. Review of priority lists will occur every six years. In addition, the minimum time required between a contaminant being listed as a regulatory determination priority and limits for that compound being set is also six years. Thus if MTBE becomes listed as a regulatory determination priority at the next opportunity in 2005, it is not likely to become a regulated contaminant until 2011. Therefore, in the near future, states cannot expect US EPA's regulatory guidance beyond the current suggested, but unenforceable, advisory level (20-40 $\mu\text{g L}^{-1}$) (10).

Currently no enforceable standards for MTBE at the state level have been established. Since 1991 DHS has maintained an interim Action Level of $35 \mu\text{g L}^{-1}$ (12). In 1997 legislation required DHS to set secondary and primary standards by July of 1998 and 1999, respectively (13,14). In California, secondary standards are enforceable and in the case of MTBE will be based on organoleptic effects (taste and odor). Minimum levels of odor and taste detection have been reported to range from $2.5\text{-}21 \mu\text{g L}^{-1}$ and $2\text{-}45 \mu\text{g L}^{-1}$, respectively (12). The primary standard for MTBE will be based on a risk assessment conducted by the Office of Environmental Health Hazard Assessment at the California Environmental Protection Agency, as well as consideration of the technical feasibility and cost of compliance. A draft of the risk assessment currently proposes $14 \mu\text{g L}^{-1}$ as the primary standard being the level producing *de minimus* risk (1 additional cancer per 1,000,000 lifetime exposures) (15). The draft proposed standard is based on three positive animal cancer studies, one ingestion study in male and female rats (16,17), one inhalation study in a different strain of male rats (18,19), and one inhalation study in male and female mice (19,20). Thus, California will soon establish enforceable standards for MTBE that are likely to be in the range of, or lower than, the lower limit of the US EPA health advisory.

1.5. Physical Properties of MTBE Influencing Environmental Fate and Transport

Several physical and chemical properties of MTBE greatly influence its fate and transport in the subsurface. In general, MTBE may occur at high concentrations in groundwater impacted by gasoline releases. When compared to benzene, it is expected to be more soluble, mobile, and much more recalcitrant in the subsurface.

Due to its high water solubility and high concentration in reformulated gasoline, concentrations of MTBE in groundwater can be substantial. The solubility of pure MTBE is an order of magnitude greater than that of benzene, approximately $50,000,000 \mu\text{g L}^{-1}$ versus $1,780,000 \mu\text{g L}^{-1}$ (21). Similarly, its mole fraction in California reformulated gasoline is an order of magnitude higher than that of benzene, approximately 0.12 versus 0.015. Thus, MTBE and benzene concentrations in water fully saturated with California reformulated gasoline may be as high as $\sim 6,000,000 \mu\text{g L}^{-1}$ and $\sim 27,000 \mu\text{g L}^{-1}$, respectively, based on methodology provided by the Office of Science and Technology Policy (OSTP) (21).

Because MTBE has an extremely low affinity to soils, it is expected to be present in the dissolved state and transported at local groundwater velocities. According to the organic-carbon-based partition coefficients close to 11 and 80 for MTBE and benzene, respectively, sorption of MTBE is expected to be an order of magnitude less significant for MTBE, relative to benzene. Thus, little significant retardation of MTBE relative to benzene may occur during their transport in the saturated zone (21).

In general, MTBE (and other alkyl ether fuel oxygenates) biodegrade much less readily than benzene. To date, field data and microcosm studies indicate that MTBE may be resistant to intrinsic biodegradation at the majority of LUFT sites. (See section 6.0)

1.6. Project Overview

The increased use of MTBE in gasoline products has resulted in numerous point source releases to shallow groundwater throughout California. Knowledge of the current and future spatial extent and/or transport of MTBE plumes in groundwater at leaking underground fuel tank (LUFT) sites is needed to address potential impacts to drinking water resources and to manage groundwater resources accordingly.

The goal of the MTBE project at LLNL is an evaluation of the potential impact of MTBE in groundwater throughout California. In this work, we are utilizing water chemistry and site data collected for compliance with present LUFT regulations (22). There are inherent limitations in the data gathered at real world LUFT sites in California and elsewhere. Limitations routinely encountered when studying the fate of MTBE and BTEX plumes utilizing extant data include: (a) monitoring networks that are much more limited than those of research field investigations, (b) multiple releases containing different gasoline formulations may have occurred at the same site, (c) release dates are unknown, and (d) mass estimates of the releases are uncertain. In addition, MTBE plume evolution is subject to multiple sources of variability such as geological heterogeneity and hydrological fluctuations in groundwater surface elevation and groundwater gradient (magnitude and direction). Therefore, data from individual sites, collected for regulatory compliance, is grossly insufficient for precise and quantitative contaminant transport research.

In contrast, laboratory studies and controlled field experiments are designed with precise, accurate, and relevant measurements and known release scenarios to test very specific hypotheses of individual mechanisms and aspects of contaminant transport. This approach has the advantage of producing definitive results. Unfortunately, by focusing on controlled situations the magnitude of real world variability, uncertainty and complexity is sometimes overlooked. This is the archetypical quandary of environmental management. While sophisticated science is abundant, environmental decision making often occurs enveloped by an unavoidable scarcity of confident information. In this work we present analysis of data from real world gasoline releases. To address the inherent limitations in data from any one site, we have analyzed data from populations of LUFT sites to elucidate general trends in the behavior of MTBE, total petroleum hydrocarbons (TPH) and benzene, ethylbenzene, toluene, xylene (BTEX) plumes.

The focus of this work is to investigate field data in order to gain insight into what is actually occurring at a large number of regulated LUFT sites with respect to both dissolved MTBE and BTEX plumes. Monitoring for MTBE at LUFT sites has been required only since July 1996, whereas data on BTEX concentrations often have been collected for many years. As a result, at most LUFT sites throughout California, sufficient MTBE data for even the simplest statistical and time-series analyses are just now becoming available. As additional data are accumulated and analyzed, the extent and impact of MTBE in groundwater will gain increasing clarity.

Results presented here are the initial findings of an ongoing study. First, because we are analyzing field data submitted for regulatory compliance, it was necessary to test limitations and validity of standard EPA analytical methods routinely used to measure MTBE concentrations. At the request of the SWRCB (June 1998), the analytical methods study was expanded to include other alkyl ether fuel oxygenates. Therefore, we have investigated the performance of EPA Method 8020A/21B, EPA Method 8260A, and a modified ASTM Method D4815 in detecting and quantifying fuel oxygenates in environmental samples from LUFT sites. Second, we have measured the occurrence of MTBE in groundwater at 236 California LUFT sites and the occurrence of MTBE impacts to California's public drinking water wells. Third, we have analyzed data from this population of LUFT sites to gain insights into the spatial distribution of MTBE plumes in California. We compared dissolved benzene and MTBE plumes lengths among a population of sites, and estimated the distribution of dissolved benzene and MTBE plumes at individual LUFT sites. Fourth, in order to examine the behavior of MTBE plumes in greater detail, we have analyzed data from 29 sites located in San Diego County where MTBE monitoring data extend from the beginning of 1992 through the end of 1996.

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2. Evaluation of EPA and ASTM Methods for Analysis of Oxygenates in Gasoline-Contaminated Groundwater

2.1. Introduction

Several oxygenates can be added to gasoline to comply with state and federal air quality requirements. Among the various fuel oxygenates, methyl *tertiary*-butyl ether (MTBE) is primarily used; other oxygenates are added in minor fractions when compared with MTBE. In California, refiners report current limited use of ethanol, periodic limited use of *tertiary*-amyl methyl ether (TAME), and past minor use of ethyl *tertiary*-butyl ether (ETBE) (1). Methanol and *tertiary*-butyl alcohol (TBA) can also be present as impurities in MTBE (1). Use of diisopropyl ether (DIPE) has not been reported in California (1).

Management of petroleum releases from leaking underground fuel tank (LUFT) sites requires monitoring of oxygenate and gasoline compounds in groundwater and, in the extreme case, nonaqueous phase liquid (NAPL) samples. Presently, US EPA Methods 8020A/21B and 8260A are used for this task (2, 3, 4). A modified version of ASTM Method D4815 has been proposed recently as an alternative technique (5). All use purge & trap (P&T) as the means of sample introduction and gas chromatography (GC) for analyte separation. Major differences exist among system configurations and detector types used.

EPA Methods 8020A and 8021B rely on photo ionization detectors (PIDs) for identification and quantitation of non-halogenated compounds (2,3). For simplicity and due to their similarities, these methods are referred to as Method 8020A/21B hereafter. Since PIDs are non-specific detectors, data of high quality can only be obtained following complete separation of target analytes (oxygenates) from signal-producing interferences (gasoline) in the GC column. Standard PID lamps (10 eV) emit sufficient energy to ionize certain saturated hydrocarbons (alkanes) such as MTBE. However, unsaturated compounds containing one or more double bonds yield much stronger responses and may represent potent sources of interference. In addition, high concentrations of saturated hydrocarbons may also cause significant PID detector interference. Therefore, false-positive identification and/or severe over-estimation of analyte concentrations may occur when analytes and interferences enter the detector cell at the same time (co-elution).

EPA Method 8260A is a more definitive (and more expensive) technique employing mass spectrometry (MS) for analyte detection. Upon bombardment with electrons, organic chemicals disintegrate into unique mass fragments and/or fragment patterns allowing unambiguous detection and quantitation of target compounds even if co-elution with interfering compounds occurs.

The two-dimensional ASTM Method D4815 was originally developed to monitor methanol, ethanol, and various ether-based oxygenates in finished gasoline (commercial product of proprietary formulation) (6). Samples are directly injected into a gas chromatograph equipped with two different columns in which the flow direction can be reversed via a set of switching valves. The primary column has polar characteristics and retains oxygenate compounds whereas hydrophobic gasoline components are vented off. Upon reversal of the flow direction, analytes are back-flushed into a non-polar, analytical column for compound separation. Analytes exiting from this secondary column are detected and quantified by means of a non-specific flame ionization detector (FID). The direct injection step may be replaced with P&T sample introduction yielding a modified method featuring enhanced detection limits for aqueous samples (5). The latter has been approved recently by the Department of Toxic Substances Control (DTSC) as an alternative method for the analysis of oxygenates in NAPL, water, and soil. In contrast to Methods 8020A/21B and 8260A, this method includes methanol and ethanol as target analytes but excludes analysis of benzene, toluene, ethylbenzene, and xylenes (BTEX) as well as total petroleum hydrocarbons (TPH).

The present work was aimed at characterizing the sensitivity of standard methods to sample matrix effects. Special attention was paid to EPA Method 8020A/21B due to its wide-spread use and previous work (7) showing that oxygenate analysis may be impacted significantly in the presence of moderate to high concentrations of gasoline ($> 1,000 \mu\text{g L}^{-1}$).

2.2. Methodology

Participating laboratories. The present study involved one research group and two commercial laboratories. EPA Method 8020A/21B was evaluated by the Environmental Restoration Division of the Lawrence Livermore National Laboratory, LLNL, Livermore, CA. EPA Method 8260A and ASTM Method D4815, respectively, were tested at AN/EN of Marina, CA, and Global Geochemistry (GGC) of Canoga Park, CA.

MDL study. Method detection limits (MDLs) were determined by analyzing seven replicates of deionized water samples containing low concentrations of analytes, calculating the standard deviation of the measurements, and multiplying the latter with the appropriate t-test value (3.14 at a 99% confidence level). In order for an MDL to be accepted, the calculated value had to be equal or greater than one tenth of the spiking level used.

PE sample analysis. Performance evaluation (PE) samples were prepared freshly by addition of 20 μL of distributed, methanolic stock solutions to 100 mL of clean (organic-free), deionized water. Samples were analyzed immediately. PE samples #1 to #5 were prepared from fresh (non-degraded, non-oxygenated) American Petroleum Institute gasoline (lot number API 91) provided by Environmental Resource Associates of Arvada, CO. Samples #6 and #7 (NAPL) were prepared from non-oxygenated Iowa State gasoline. PE samples were analyzed in duplicate yielding information on analysis precision, *i.e.*, closeness of two independent measurements to each other regardless of the

actual value (reported as relative percent deviation, RPD), and accuracy, *i.e.*, closeness of measured values to actual concentrations in the sample (reported as percent accuracy, where 100 percent represents an ideal measurement). Concentrations are expressed in $\mu\text{g L}^{-1}$. Samples containing $\geq 50,000 \mu\text{g L}^{-1}$ of gasoline were diluted by the analysts as required; in the case of Method 8020A/21B, TPH concentrations were reduced to approximately $5,000 \mu\text{g L}^{-1}$. Final compositions of the individual PE samples are listed in Table 2.1.

Table 2.1. Composition of performance evaluation (PE) samples.

PE Sample #	API Gasoline, [$\mu\text{g L}^{-1}$]	Oxygenates [$\mu\text{g L}^{-1}$]
1	None	+
2	500	+
3	5,000	+
4	50,000	+
5	50,000	None
6	NAPL	None
7	NAPL	2,000,000 each**

(+) Spiked with $35 \mu\text{g L}^{-1}$ of MTBE, TAME, DIPE, ETBE and $500 \mu\text{g L}^{-1}$ of TBA.

NAPL= nonaqueous phase liquid

** = MTBE, TAME, DIPE, ETBE and TBA

2.3. Results

Mass fragments of oxygenates. During analysis of chemical standards by Method 8260A, characteristic mass fragments were identified for each of the five oxygenate compounds (Table 2.2); these fragments served for compound identification and quantitation.

Table 2.2. Characteristic mass fragments of oxygenates.

Analyte	Ion, (m/z)
TBA	59
MTBE	73
DIPE	87
ETBE	87
TAME	73

(m/z) Mass-to-charge ratio

MDL studies. MDLs were determined in three different matrices including clean water (organic-free reagent water), water containing 5,000 $\mu\text{g L}^{-1}$ of non-oxygenated gasoline, and undiluted, non-oxygenated gasoline (NAPL) (Table 2.3). In clean water at ambient temperature, detection limits for ether oxygenates were on the order of 1 $\mu\text{g L}^{-1}$ regardless of the method used; MDLs for TBA were about one order of magnitude greater (13.9 to 34.9 $\mu\text{g L}^{-1}$). Sensitivity of Method 8260A for analysis of MTBE and TBA was increased by approximately one order of magnitude by use of greater sample volumes (10 vs. 5 mL) and higher sample temperatures (40° vs. 20°C) (Table 2.3A). In the presence of 5,000 $\mu\text{g L}^{-1}$ of gasoline, MDLs of Method 8020A/21B increased by a factor of 5 to 10, whereas detection limits for Method 8260A did not change considerably (Table 2.3B). Similarly, detection limits of Method D4815 were insensitive to the presence of 5,000 $\mu\text{g L}^{-1}$ of gasoline; in free product, minimum detectable analyte concentrations ranged from 10,200 to 43,600 $\mu\text{g L}^{-1}$ (Table 2.3C).

Table 2.3. Method detection limits of oxygenate compounds in various sample matrices by standard method used.

A. Reagent water.

Analyte [$\mu\text{g L}^{-1}$]	EPA Method 8020A/21B	EPA Method 8260A		Modified ASTM Method D4815
	(5 mL; 20°C)	(5 mL; 20°C)	(10 mL; 40°C)	(5 mL; 20°C)
TBA	13.9	34.9	3.0	27.4
MTBE	0.2	1	0.2	1.1
DIPE	0.2	0.5	0.1	1.1
ETBE	0.2	0.6	0.2	0.9
TAME	0.2	0.6	0.1	0.7

B. Water containing 5,000 $\mu\text{g L}^{-1}$ of gasoline.

Analyte [$\mu\text{g L}^{-1}$]	EPA Method 8020A/21B	EPA Method 8260A	Modified ASTM Method D4815
	(5 mL; 20°C)	(10 mL; 40°C)	(5 mL; 20°C)
TBA	195.5	4.6	39.7
MTBE	1.2	0.3	1.2
DIPE	1.6	0.3	1.1
ETBE	5.5	0.3	1.2
TAME	1.2	0.2	1.2

C. Nonaqueous phase liquid (NAPL).

Analyte [$\mu\text{g L}^{-1}$]	Modified ASTM Method D4815 (Direct Injection; 20°C)
TBA	40,800
MTBE	43,600
DIPE	22,600
ETBE	10,200
TAME	16,100

Analysis of oxygenates in dissolved gasoline matrices. The precision of analysis was good throughout the study independent of sample matrix, target analyte and type of analysis used; typical RPDs were in the order of 1 to 8% (data not shown). However, the accuracy of analysis was strongly affected by the specific analysis conditions. Accuracy of TBA analysis varied with method and system configuration (Figure 2.1). Methods D4815 and 8260A yielded accurate results over a broad range of TPH concentrations (0 to 50,000 $\mu\text{g L}^{-1}$). In contrast, Method 8020A/21B produced unacceptable TBA values (421 to 1381% recovery) when TPH concentrations exceeded 500 $\mu\text{g L}^{-1}$ regardless of the column type and sample temperature used.

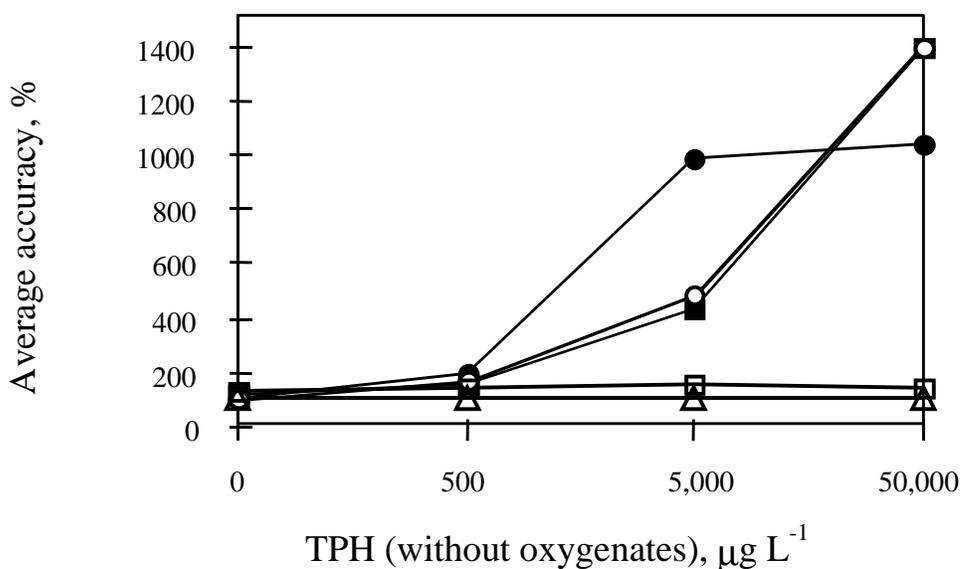


Figure 2.1. Average accuracy of *tertiary*-butyl alcohol (TBA @ 500 $\mu\text{g L}^{-1}$) analysis as a function of total petroleum hydrocarbon (TPH) concentration. Plot shows results obtained with Method 8020A/21B (Rtx-5 column, 20°C, (●), and 40°C, (○)); DB-MTBE column, (20°C, (■)), Method 8260A (20°C, (□)), and the modified Method D4815 (20°C, (Δ)). See Appendix 2-A for column details.

In comparison to the analysis of TBA, determination of ether oxygenates was more accurate. Results obtained for MTBE, ETBE, DIPE, and TAME were similar and are presented in a summary plot showing average accuracy of analysis as a function of TPH content (Figure 2.2). All methods yielded acceptable or even excellent results for samples containing up to 5,000 $\mu\text{g L}^{-1}$ of gasoline. However, the average accuracy of Method 8020A/21B was severely impacted when samples with high TPH concentrations (50,000 $\mu\text{g L}^{-1}$) were analyzed at elevated sample temperature (40°C).

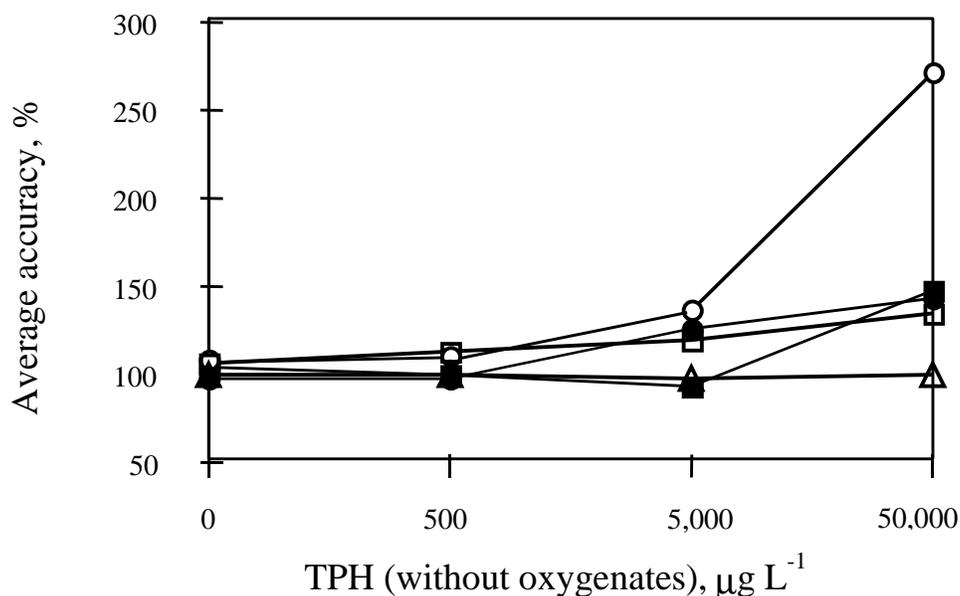


Figure 2.2. Average accuracy of ether oxygenate analysis (MTBE, ETBE, DIPE, and TAME @ 35 $\mu\text{g L}^{-1}$) as a function of TPH concentration. Plot shows results obtained with Method 8020A/21B (Rtx-5 column: 20°C, (●), and 40°C, (○)); DB-MTBE column: (20°C, (■)), Method 8260A (20°C, (□)), and the modified Method D4815 (20°C, (△)). See Appendix 2-A for column details.

In the presence of gasoline interferences, Method 8020A/21B yielded high quality data only when appropriate settings for retention time (RT) windows were selected. RT windows of 24 seconds duration are frequently used in commercial laboratories (RT \pm 0.2 minutes). Accordingly, all presented data were generated using this value. When tighter peak windows were selected (RT \pm 0.75 to 1.5%), analysis of gasoline-containing samples frequently produced false-negative results for all target analytes while typical quality assurance and quality control (QA/QC) standards passed without problems (data not shown).

False-positive misidentification of oxygenates. The potential and severity of false-positive misidentification of compounds was determined in deionized water containing 50,000 $\mu\text{g L}^{-1}$ of conventional, non-oxygenated gasoline (PE sample #5). No false-positive misidentification occurred with Method 8260A, whereas one minor false-positive misidentification of ETBE was observed with Method D4815 yielding a concentration close to the detection limit. In contrast, frequent false-positive misidentifications of all analytes were found when Method 8020A/21B was used to analyze samples containing high concentrations of gasoline (Table 2.4).

Table 2.4. Average tendency and magnitude of false-positive misidentification of oxygenates in water (5 mL) containing 50,000 $\mu\text{g L}^{-1}$ of conventional gasoline (PE sample #5).

Method	Run Conditions	TBA [$\mu\text{g L}^{-1}$]*	MTBE [$\mu\text{g L}^{-1}$]*	DIPE [$\mu\text{g L}^{-1}$]*	ETBE [$\mu\text{g L}^{-1}$]*	TAME [$\mu\text{g L}^{-1}$]*
8020A/21B**	Rtx-5, 20°C	12,289	32	35	16	2
“	Rtx-5, 40°C	6,905	38	125	65	17
“	DB-MTBE, 20°C	12,203	38	<2	99	56
8260A	5 mL, 20°C	<250	<20	<10	<10	<10
D4815	20°C	<40	<2	<2	3	<2

(*) Data represent average values of two independent measurements.

(**) Refer to Appendix 2-A for specification of column dimensions and run conditions.

Method 8020A/21B yielded unacceptable, false-positive results for TBA in the presence of significant quantities of gasoline interferences. Misidentification of this compound was severe, producing average false-positive concentrations between 6,905 and 12,289 $\mu\text{g L}^{-1}$ regardless of the column type used. In contrast, false-positive values for all other oxygenates were much lower with values ranging from 2 to 125 $\mu\text{g L}^{-1}$. With respect to the analysis of DIPE, use of the DB-MTBE column (see Appendix 2-A for column dimensions) was beneficial, resulting in a true, non-detect value in the 50,000 $\mu\text{g L}^{-1}$ gasoline sample.

Analysis of oxygenates in NAPL. The applicability of the different methods for the analysis of oxygenates in NAPL samples was also tested (PE samples #6 and #7, see Table 2.1 for sample composition). Use of Method 8020A/21B resulted in false-positive misidentifications of all analytes, as well as over-estimation of actual concentrations, that, in the case of TBA, produced meaningless values (concentrations $\geq 1 \text{ Kg L}^{-1}$; data not shown). Methods 8260A and D4815 yielded high quality data with no false-positive results and average recoveries ranging from 92 to 130% (data not shown).

2.4. Discussion and Conclusions

EPA Method 8020A/21B is an inexpensive tool routinely employed for monitoring of BTEX and TPH concentrations in groundwater samples from LUFT sites. The present study focused on the applicability of this and two alternative methods to the analysis of fuel oxygenates in simulated field samples. Major findings are summarized in Table 5.

Table 5. Applicability of standard methods to the analysis of oxygenates samples from LUFT sites.

Sample Matrix	Method 8020A/21B*	Method 8260	Modified Method D4815
Clean water	+	+	+
500 $\mu\text{g L}^{-1}$ gasoline	+	+	+
5,000 $\mu\text{g L}^{-1}$ gasoline	a	+	+
50,000 $\mu\text{g L}^{-1}$ gasoline	b	+	+
NAPL	-	±	+

(*) Not suggested for TBA analysis.

(+) Good results regardless of instrument settings.

(±) Yields good results when oxygenate concentrations $\geq 2,000,000 \mu\text{g L}^{-1}$.

(-) Method not applicable.

(a, b) Method performance dependent on instrument settings and TPH-to-analyte ratio. Results of this study indicate that MDLs determined in clean water are unrealistically low resulting in frequent false-positive misidentification of ether oxygenates especially when analyzing for low levels of ether oxygenates in the presence of gasoline. Laboratories are advised to determine MDLs in a gasoline matrix or to raise the limits of detection until analysis of a “matrix blank” containing maximal amounts of non-oxygenated gasoline yields a non-detect value for all ether oxygenates. In this study, MDLs determined in clean water needed to be increased by as much as a factor of 28 (a) and 280 (b) in order to prevent false-positive misidentification. These results cannot be broadly generalized and must be verified by individual laboratories for each EPA Method 8020A/21B set-up.

Method 8020A/21B

Several problems were encountered when using Method 8020A/21B for analysis of TBA. Method detection limits for this compound were relatively high due to TBA’s poor purging efficiency, and the weak response it yielded with the standard 10 eV PID lamp. Further, the accuracy of analysis was extremely poor in the presence of gasoline because TBA was not well retained and thus co-eluted with low-boiling gasoline interferences in the GC columns tested. Analysis at elevated sample temperature (heated purge) was expected to increase the sensitivity of analysis but actually was counter-productive. At 40°C, both TBA and interferences were transferred more effectively from the water sample into the GC column yielding less accurate results when compared to data obtained at ambient temperature. Taken together, these findings suggest that TBA analysis by Method 8020A/21B is unreliable and especially error-prone when analyzing LUFT samples containing gasoline.

In this study, the ether oxygenates MTBE, ETBE, DIPE, and TAME were monitored by Method 8020A/21B with sufficient sensitivity and accuracy in aqueous samples containing up to 5,000 $\mu\text{g L}^{-1}$ of gasoline. Under configurations tested, this method produced very conservative results as indicated by a lack of false-negative

misidentifications, and a tendency for both over-estimation of analyte concentrations and false-positive detections.

Although this study aimed to mimic instrumentation and operating parameters frequently used in commercial laboratories, findings cannot be generalized easily, because standards for the many variables influencing the quality of analysis either do not exist or are not strictly enforced. For example, a 1996 survey of 16 commercial laboratories revealed that GC columns used in commercial laboratories for Method 8020A/21B may vary in length from only 10 meters up to 75 meters, with the majority of laboratories (75%) using 30-meter megabore columns (0.53 mm inner diameter) similar to those tested in this work (7). Both columns tested produced comparable results with respect to the accuracy and precision of analysis and differed only slightly regarding their potential for false-positive detection of individual ether oxygenates. Thus, the dimensions of the GC column may be more important than its specific type of inner coating. The fact that chromatographic limitations (*i.e.*, the inability to separate analytes from co-eluting gasoline compounds) were already apparent with the 30-meter columns tested in this study encourages the use of longer ones. However, choosing appropriate hardware is by no means a guarantee for high data quality. Results presented in Table 2-B of the Appendix indicate that commercial laboratories may employ columns as long as 75 meters and still produce erroneous data if operating parameters are not selected carefully (7). Conversely, a laboratory using 30-meter columns may outperform a competitor employing longer columns if instrument settings such as retention time windows, etc. are chosen scrupulously.

With respect to operating parameters, the selection of appropriate peak windows was identified as an especially important factor determining the quality of analysis. Windows needed to be broad enough (average RT \pm 0.2 min) to accommodate retention time shifts caused by gasoline interferences. While peak windows with a total width of 0.4 minutes appear to be representative for many laboratories, it cannot be ruled out that, in some cases, analysts use tighter settings in conjunction with electronic pressure control (EPC). EPC can minimize retention time shifts caused by instrument and pressure variations; however, it cannot eliminate variations resulting from heavy loading of the GC column with gasoline interferences (matrix effects). Thus, excessively tight peak windows may cause erroneous data (*i.e.*, frequent false-negative misidentifications) during the analysis of gasoline-containing samples. In practice this does not appear to be a problem, however. An evaluation of data from commercial analytical laboratories found false-negative results for MTBE to be rare. Specifically, out of 144 groundwater samples containing $> 1,000 \mu\text{g L}^{-1}$ of TPH only one yielded a false-negative result when analyzed by EPA Method 8020A/21B (7).

Frequent false-positive misidentification of oxygenates in samples containing $50,000 \mu\text{g L}^{-1}$ of non-oxygenated gasoline underscored the problems associated with the current practice of defining MDLs for Method 8020A/21B. Results of this study indicate that limits of detection for oxygenates increase in the presence of $5,000 \mu\text{g L}^{-1}$ of gasoline by as much as a factor of 28 when compared to values obtained in clean water (compare Tables 3A and 3B). Current EPA protocols do not account for this phenomenon. Additional data not presented indicate that the analysis of samples containing

5,000 $\mu\text{g L}^{-1}$ of non-oxygenated gasoline can result in false-positive misidentifications of ether oxygenates on the order of about 10 $\mu\text{g L}^{-1}$. Thus, false-positive misidentification and over-estimation of oxygenate concentrations may be common in commercial laboratories, especially when analyzing low levels of ether oxygenates in gasoline-containing samples (see Table 2-B in the Appendix).

The quality of data produced by Method 8020A/21B could be enhanced easily by determining MDLs for oxygenates in a more realistic fashion. Ideally, laboratories should measure MDLs by analyzing seven replicates of gasoline-containing samples spiked to low levels with oxygenates as done in this study. The amount of non-oxygenated gasoline used should be equivalent to the maximum column capacity (recoveries of surrogate standards will fail to comply with QA/QC criteria when the column capacity is exceeded). MDLs presented in Table 2.3B were determined accordingly. In practice, these values would be multiplied by a factor of 3 to 4 to yield the so-called “reporting limit” (the detection limit used for the purpose of reporting). If adopted by commercial laboratories, the suggested method modification would eliminate most of the currently observed false-positive misidentifications and raise the reporting limits for ether oxygenates. For the instrumentation and settings tested in this study, calculated reporting limits were approximately 4 to 6 $\mu\text{g L}^{-1}$ for MTBE, DIPE, and TAME and about 20 $\mu\text{g L}^{-1}$ for ETBE. Reporting limits for samples containing large amounts of gasoline will be even higher due to adjustment for dilution required prior to analysis. In the majority of cases, these more realistic reporting limits should be low enough to qualify Method 8020A/21B as a suitable tool for routine monitoring at LUFT sites.

Alternatively or as an added measure of safety, laboratories may decide to include an additional check sample into their daily QA/QC routine to avoid potential false-positive misidentifications of ether oxygenates. Specifically, an oxygenate-free “matrix blank” (additional method blank) containing gasoline at concentrations equivalent to the individual column capacity should be analyzed and MDLs for oxygenates raised until a non-detect value is obtained for all ether compounds. This “matrix blank” would also be appropriate to confirm detection and/or reporting limits of oxygenates determined in a gasoline matrix as described above.

Until Method 8020A/21B undergoes necessary modifications, the concentration ratio of TPH (less oxygenates) to analyte can be a helpful parameter when assessing the potential quality of past and present data reporting the occurrence of ether oxygenates at LUFT sites. For GC configurations tested in this study, Method 8020A/21B yielded excellent results when monitoring 35 $\mu\text{g L}^{-1}$ of ether oxygenates in sample matrices containing no or only small amounts of gasoline (0 and 500 $\mu\text{g L}^{-1}$, respectively) but data became increasingly unreliable, when the ratio of TPH-to-oxygenate content increased (as observed in samples containing 5,000 and 50,000 $\mu\text{g L}^{-1}$ of oxygenates, respectively). Thus, oxygenate concentrations determined in groundwater samples by Method 8020A/21B may be less dependable when the fuel additive contributes only a small fraction (less than about 7%) to the total TPH concentration reported for the sample. This

will be especially true if oxygenates were detected at levels close to detection limits derived from clean water matrices.

The databases used in this study for characterization of the behavior of MTBE at LUFT sites were also affected by the above limitations of EPA Method 8020A/21B. The reader should refer to Appendix 2-C for a brief discussion of data quality and its potential effects on the validity of results obtained in this study.

It should be noted that the PE samples analyzed in this study were prepared from fresh, conventional gasoline. Weathered or partially degraded fuel may cause slightly different analytical effects when analyzed by Method 8020A/21B, due to either attenuated concentrations of specific gasoline components or the presence of additional compounds (metabolites) produced during incomplete biodegradation of gasoline.

Method 8260A

Method 8260A was reliable when analyzing oxygenates in samples with high TPH content yielding excellent results under all test conditions for all alkyl ether fuel oxygenates and TBA. In contrast to Method 8020A/21B, use of elevated sample temperature (40°C vs. 20°C) was beneficial for TBA analysis. During heated purge, compounds were more effectively transferred to the mass spectrometer, which could resolve target analytes from potentially interfering gasoline components. Analysis of oxygenates in NAPL samples by Method 8260A was successful because analyte concentrations were sufficiently high (2,000,000 $\mu\text{g L}^{-1}$ for each oxygenate) allowing substantial dilution of the samples prior to analysis without reducing oxygenate concentrations below detectable levels (dilution factor: 100,000; MDLs: ~2,000,000 $\mu\text{g L}^{-1}$).

Method D4815

Method D4815 was the preferred tool for analysis of NAPL samples, due to its low detection limits. In addition, it yielded excellent results under all test conditions for all alkyl ether fuel oxygenates and TBA when aqueous samples were analyzed by P&T sample introduction. Its reliability and resilience to gasoline interferences were exceptional considering the use of a non-specific detector (FID). Limitations of this method include its restricted commercial availability, and the need for additional analyses for quantitation of BTEX and TPH concentrations.

2.5. Recommendations

Since Method 8020A/21B is quite sensitive to operational parameters (*i.e.*, column dimensions and RT window settings) when analyzing gasoline-containing samples for oxygenates, it is difficult to make a general statement regarding the quality of data currently provided by commercial laboratories. However, most of the uncertainties presently associated with Method 8020A/21B could be eliminated with slight method modifications.

1. **Misidentification of ether oxygenates needs to be minimized by raising MDLs to more realistic values.** As outlined above, laboratories should measure oxygenate MDLs in aqueous samples containing non-oxygenated gasoline at levels equivalent to the individual column capacity (excessive column loading will be indicated by surrogate standard recoveries that fail QA/QC criteria). These MDLs should be verified by inclusion of an additional check sample into the daily QA/QC procedure. In contrast to the method blank defined by EPA, this “matrix blank” should contain conventional, non-oxygenated gasoline at concentrations equivalent to the GC column capacity. If necessary, MDLs determined in the gasoline matrix need to be raised until a non-detect value is obtained for all ether oxygenates when analyzing this check sample. Unfortunately, this “matrix blank” cannot substitute the (clean water) method blank defined by the EPA because conventional gasoline contains several target analytes listed for Method 8020A/21B.
2. **The current practice of preparing matrix spike samples from clean water needs to be abandoned.** Instead, duplicate matrix spike samples (as defined by EPA protocols) should consist of an aqueous matrix containing conventional, non-oxygenated gasoline at concentrations equivalent to the maximum column capacity. This matrix should be spiked with oxygenate compounds to action levels specified by the State and analyzed. Results will indicate whether the employed hardware and operating conditions are appropriate for separation and detection of target compounds in complex, gasoline-containing samples.
3. **In the absence of regulatory requirements to adopt these method modifications, clients should decide to either submit check standards (as described above) to their contract laboratories for quality control or to utilize only those laboratories that voluntarily adopt the specified procedures.**
4. In many situations, Method 8020A/21B may be appropriate for routine monitoring of ether oxygenates (MTBE, DIPE, ETBE, and TAME) at LUFT sites due to its typically conservative nature, *i.e.*, its tendency to produce false-positive rather than false-negative results. However, in the absence of regulatory requirements to adopt additional QA/QC criteria to ensure the reliability of Method 8020A/21B, **more definitive tests such as EPA Method 8260A and ASTM Method D4815 are recommended when monitoring oxygenates in samples that may have high regulatory impact.** These situations could include monitoring for low levels of alkyl ether fuel oxygenates in:

- downgradient boundary wells with high TPH concentrations;
- temporary boring samples obtained from areas of the plume potentially containing high gasoline concentrations;
- NAPL samples.

5. Method 8020A/21B should not be used for the analysis of TBA. Alternative candidates include Method 8260A, ASTM Method D4815 or equivalent.

2.6. Acknowledgments

We would like to thank Sarah R. Schoen from AN/EN of Marina, CA, as well as Yakov Galperin and Isaac R. Kaplan from Global Geochemistry of Canoga Park, CA for their participation in this study. We also wish to thank the LUFT Methods Committee of the Department of Toxic Substances Control for invaluable discussions and for input and advice over the scope of this work.

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2.8. Appendix

Table 2-A. Instrument configurations and run conditions used for EPA Method 8020A/21B.

Specifications (Column type)	8020A/21B (Rtx-5)	8020A/21B (DB-MTBE)
Carrier gas, flow rate	Helium, 10 mL/min	Helium, 10 mL/min
Column dimensions	30 m x 0.53mm x 3 µm	30 m x 0.53mm x 3 µm
Temperature programming	6 min @ 35°C, 4°C/min to 90°C, 10°C/min to 180°C, up to 5min@180°C	6min @ 35°C, 12°C/min to 190°C, 3 min @ 190°C
Run time	28.75 to 33.75 min	21.92 min
Injector type	O/I Low dead volume	O/I Low dead volume
Injector temperature	160°C	160°C
Detector type	O/I PID	O/I PID
Detector temperature	200°C	200°C
PID lamp	10 eVolts	10 eVolts
Trap type	Supelco 3 component trap: Tenax, silica, charcoal	Supelco 3 component trap: Tenax, silica, charcoal
Pre-heat time	N/A	N/A
Purge temperature	20°C or 40°C	20°C
Purge time	11 min	10 min
Dry purge	1 min	1 min
Desorb preheat	1 min to 175°C	1 min to 175°C
Desorb time	2 min	2 min
Desorb temperature	180°C	180°C
Bake time	15 min	10 min
Bake temperature	200°C	200°C
Water management system	On	On
Transfer line temperature	120°C	120°C
Valve temperature	120°C	120°C

Table 2-B. Testing for false-positive identification of MTBE. Analysis of 1,300 $\mu\text{g L}^{-1}$ API non-oxygenated gasoline by sixteen commercial laboratories.

Laboratory	MTBE ($\mu\text{g L}^{-1}$)			Primary Column			Secondary Column		
	Primary Column	Secondary Column	Reporting Limits	Type	Length (m)	Diameter (mm)	Type	Length (m)	Diameter (mm)
1	<1	7.7	1	DB624	15	0.53	DB1	15	0.53
2	8	-	5	DB-5	30	0.53	-	-	-
3	<10	<10	10	RTX-1	30	0.53	DB-URX	30	0.45
4	10	-	5	DB-624	30	0.53	-	-	-
5	<10	-	10	DB-624	30	0.53	-	-	-
6	<10	<10	10	DB-5	30	0.53	DB-VRX	30	0.45
7	<1	-	1	RTX-1	30	0.53	-	-	-
8	<5	<5	5	DB-624	75	0.45	DB-VRX	75	0.45
9	<5	-	5	DB1	30	0.53	-	-	-
10	5.5	-	4	DB624	30	0.53	-	-	-
11	10	20	5	RTX-1301	30	0.53	RTX-1	30	0.53
12	12	38	10	DB-624	30	0.53	DB-5	30	0.53
13	20	15	13	DB-624	75	0.53	DB-5	30	0.53
14	56	-	25	DB-5	30	0.53	-	-	-
15	8	-	5	Petrocal 3710	10	0.53	-	-	-
16	<5	-	5	DB-624	30	0.53	-	-	-

(-) Not Applicable

App. 2-C

This study was based on data from groundwater samples collected at a variety of California LUFT sites. Although the exact type of analysis used for individual samples is unknown, it must be assumed that the vast majority of MTBE analyses were performed by EPA Method 8020A/21B. Thus, several problems identified in Section 2.0 potentially may have affected the quality of our database. The following is a brief discussion of data quality and its potential effects on the validity of results and conclusions obtained in this study.

Section 3.2.

False-positive detections of MTBE may have artificially inflated the frequency of MTBE occurrence at California LUFT sites. In addition, cumulative distribution plots of maximum MTBE concentrations may have suffered from overestimated analyte concentrations. The portion of samples having low MTBE concentrations and containing significant quantities of TPH ($>1000 \mu\text{g L}^{-1}$) would be particularly prone to false-positive misidentification and overestimation.

Section 3.3.

MTBE analysis of drinking water is typically performed using EPA Method 502 (GC/PID) or EPA Method 524.2 (GC/MS). In general, excellent data quality can be expected, *i.e.*, neither overestimation of MTBE nor false-positive misidentifications should occur at a high frequency, because drinking water samples generally do not contain significant quantities of gasoline.

Section 4.3.

Overestimation of MTBE concentrations and false-positive detections of MTBE in downgradient monitoring wells potentially may have inflated estimates of MTBE plume lengths. In reality, this probably was not the case because, on a site-by-site basis, MTBE plumes were typically equivalent in length or only slightly shorter than their corresponding benzene plumes (defined by action levels of 20 and $1 \mu\text{g L}^{-1}$, respectively), implying that the quality of data was presumably excellent due to very small or non-detectable levels of interfering TPH in samples from downgradient monitoring wells that were used to delineate plume contours.

Section 5.3.1 and 5.3.2

False-positive detections and/or overestimation of MTBE concentrations may have affected the analysis of maximum MTBE concentration distributions. Site average concentrations may have been less affected by these errors, however (Figures 5.1 and 5.2).

Conditional probabilities of detection may have been biased toward MTBE due to false-positive misidentifications of the analyte in some samples (Figures 5.3 and 5.4).

In general, data of high quality can be expected for analysis of MTBE in monitoring wells with low TPH impacts ($<1000 \mu\text{g L}^{-1}$). Therefore, brief increases in MTBE concentrations observed in response to precipitation events were unlikely due to analytical artifacts (Figure 5.5).

Measurements of MTBE in downgradient monitoring wells were potentially error-prone only when significant quantities of gasoline compounds were present in the samples (Figure 5.6). The most elevated MTBE concentrations in this study were observed in wells with low TPH impacts and are presumed to be reliable.

False-positive misidentification of MTBE is more likely to occur in near-source wells than in downgradient wells (Figure 5.7 and 5.8). Near-source wells containing high concentrations of TPH and low concentrations of MTBE are the most prone to false-positive MTBE results. This effect would be significant in a minority of the analytical results only, because near-source wells generally have the highest concentrations of MTBE. Measurement of MTBE in samples from downgradient wells with low TPH concentrations are prone to overestimation and false-positive misidentification when the concentration ratio of MTBE to TPH is small. However, these wells generally have concentration ratios favoring accurate. Therefore, errors are expected to be limited.

3. MTBE Monitoring and Occurrence Data

3.1. MTBE Detections at California LUFT sites

The State Water Resources Control Board first requested monitoring of MTBE at all open gasoline LUFT sites in California on July 30, 1996. Prior to this, several major oil companies began monitoring for MTBE in 1995 and voluntarily submitted this information to regulatory agencies per a request by the Western States Petroleum Association. Both requests addressed the need for obtaining statewide MTBE occurrence data.

We have examined groundwater data for 236 LUFT sites located in 24 counties in California. Five major oil companies voluntarily submitted this data to the SWRCB in 1996. We have investigated the geographic distribution and geological setting of the study sites versus all LUFT sites in California. Based on the site address, geocoding information services (ETAK, Inc.) were utilized to provide the geographical locations for 226 (96%) of the MTBE study sites and 27,472 (85%) of the total California LUFT sites. Locations of LUFT sites were mapped onto the California generalized Geology Map coverage (1) in order to correlate site location with general sediment type. This analysis located greater than 80 percent of all California LUFT sites and 88 percent of the MTBE study sites in alluvial sediments (2). Therefore, the geologic setting of the MTBE study sites is expected to be representative of the majority of California LUFT sites. The majority of the MTBE study sites are located within the greater Los Angeles and San Francisco urban areas and surrounding environs. These urban areas also have the highest per county density of LUFT sites. The majority of benzene impacts to both private and public drinking water wells also cluster in these areas; however, benzene impacts have also occurred sporadically in more rural areas. By these measures, the 236 study sites appear to be generally representative of the majority of California LUFT sites in both geographic location and geologic setting.

Within these 236 sites, 78% reported detectable levels of MTBE, while 74% had maximum concentrations above $5 \mu\text{g L}^{-1}$. In addition, 70% and 10% reported MTBE detections above $20 \mu\text{g L}^{-1}$ and $10,000 \mu\text{g L}^{-1}$, respectively (Figure 3.2). Therefore, our analysis suggests that MTBE will be detected in groundwater at the vast majority of LUFT sites where petroleum hydrocarbons are present in the shallow groundwater. These results agree well with an industry study showing that MTBE is present at approximately 77% of 412 California LUFT sites as well as at essentially all sites in Maryland (98%) where MTBE has been used as an oxygenate for longer periods of time (3).

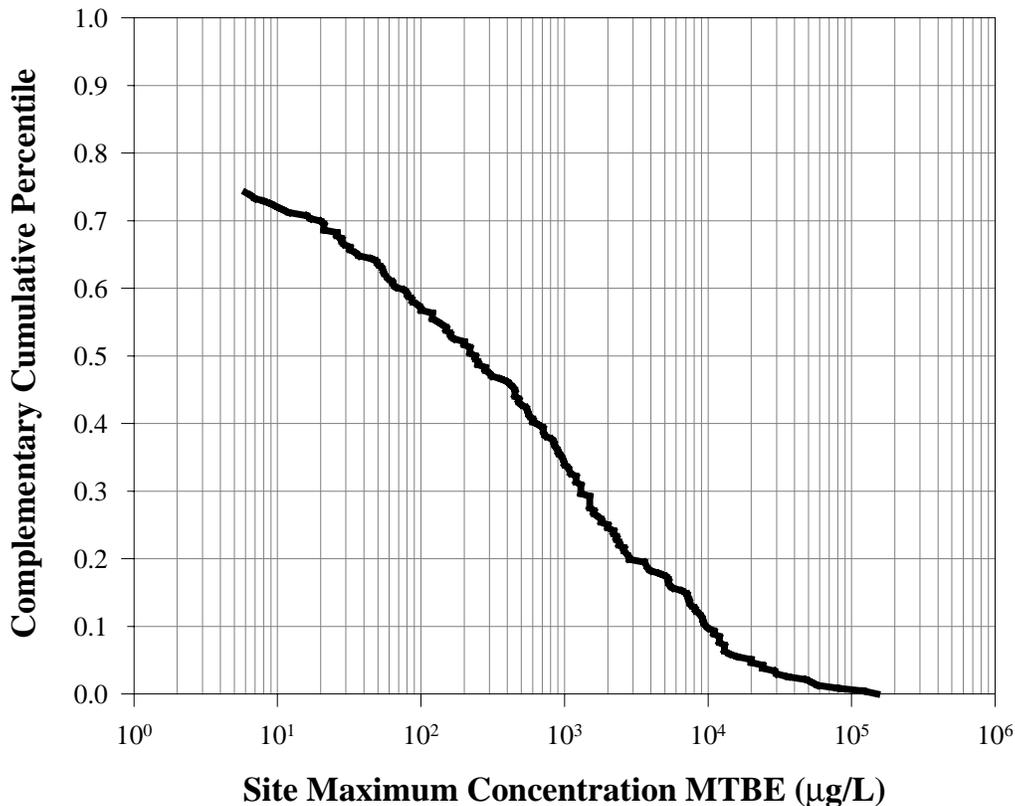


Figure 3.1. Complementary cumulative distribution of maximum MTBE concentrations at each of 236 California LUFT sites (percentile of sites with maximum concentration exceeding ordinate value). The curve includes sites for which MTBE was detected at or above 5 µg L⁻¹.

As of March 1998, 32,409 sites were regulated LUFT cases (4) in California. Among these sites, 13,278 were reported to the SWRCB as having impacted groundwater, while an additional 2,915 are noted as unknown groundwater impact and 16,216 are reported as soil-only impact (4). Given an MTBE occurrence rate of approximately 78 percent at sites where fuel hydrocarbons have impacted shallow groundwater, there may potentially be greater than 10,000 point sources of MTBE resulting from known underground storage tank releases. This may significantly underestimate the number of MTBE sources because (a) a portion of the sites classified as unknown will have impacted groundwater, and (b) the number of known LUFT sites in California is increasing as many USTs are investigated and upgraded to meet federally mandated standards by December 1998.

3.2. Monitoring and Detection of MTBE in Public Drinking Water Supplies

3.2.1 Regulatory Mandates. Testing for MTBE as an “unregulated chemical” was required by the California Department of Health Services as of February 1997, replacing a February 1996 request for voluntary monitoring (5). All groundwater supply wells within “community” and “nontransient-noncommunity” water systems are to be sampled at least once. These wells serve drinking water to at least 25 yearlong residents (or the same 25 nonresidents over 6 months per year) or have more than 15 service connections used by yearlong residents (6). Particularly vulnerable sources, defined as sources “located within 2,000 feet of a gas tank, gas pipeline, refinery or tank farm (or perhaps further depending on the local subsurface geology)”, are to be monitored for MTBE by August 31, 1998 (5). Otherwise, water suppliers may conduct their MTBE sampling concurrently with the next scheduled volatile organic compound (VOC) sampling within a three-year compliance period or within a six-year period if granted a waiver for monitoring for one or more VOCs. Monitoring for MTBE is not required, if the well is located in very remote rural areas where there are no possible point sources of contamination (5). Further, waivers for initial MTBE monitoring can be granted for up to 9 years if the well is within a small water system (< 200 connections) with fewer than 150 connections (5); these waivers could result in significant reduction of MTBE monitoring in small water systems.

Monitoring requirements for MTBE will soon change with the mandated adoption of secondary and primary drinking water standards in July 1998 and July 1999, respectively (7, 8). Currently, compliance with secondary MCLs requires monitoring every three years of all community groundwater wells, while adoption of a primary drinking water standard requires monitoring of all groundwater wells within both community and nontransient-noncommunity water systems every three years (6). In both cases, waivers for monitoring of individual VOCs may be granted based on vulnerability and/or previous monitoring results (6).

3.2.2 Analysis of MTBE Monitoring Data. We have evaluated the California Department of Health Services (DHS) drinking water databases (9, 10) as of March 1998 to determine the frequency of MTBE testing of public groundwater supply wells as well as the occurrence and concentrations of MTBE. The analysis presented in Table 3.1 is limited to public supply wells classified as active drinking water sources; these are by definition wells that are always available for use within the water system. Overall, the majority of active supply wells as reported to the DHS appear not to have been monitored for MTBE (Table 3.1).

Table 3.1. Monitoring of MTBE and benzene in California active groundwater wells within public drinking water systems.

Service Connections	Inventory		Benzene		MTBE	
	Systems with active groundwater sources	Active wells in these systems	Percent of systems tested	Percent of wells tested	Percent of systems tested	Percent of wells tested
Large Systems:						
100,000 and greater	6	490	100.0	84.9	100.0	41.6
50,000 to 99,999	9	449	100.0	89.8	77.8	31.4
25,000 to 49,999	34	655	94.1	91.0	88.2	48.9
10,000 to 24,999	106	1500	93.4	83.0	66.0	41.8
5,000 to 9,999	85	726	89.4	82.5	61.2	37.5
1,000 to 4,999	294	1646	93.2	72.4	45.6	25.8
200 to 999	361	1127	79.8	64.2	21.1	13.6
total	895	6593	87.6	78.5	41.9	32.5
Small Systems*:						
unknown to 199	2734	3661	46.3	41.8	3.1	3.3

(*) Data presented include community and nontransient-noncommunity water systems only.

MTBE Monitoring In Large Water Systems. Monitoring for MTBE as reported in the DHS water quality monitoring database appears to be generally limited to drinking water wells in large systems. Water systems with 200 or greater connections contained a total of 6593 active groundwater supply wells. Wells within systems with 5,000 or more connections showed the highest level of monitoring for MTBE (38% tested), while monitoring for MTBE decreased significantly for wells in systems with less than 5,000 connections (13 to 26% tested) (Table 3.1).

MTBE Monitoring In Small Water Systems. Community and nontransient-noncommunity water systems with 199 or less connections contained a total of 3,661 groundwater supply wells, the vast majority being single-well water systems. Individual counties manage many of these systems and chemical analysis data from the counties is not typically included in the database. Among state regulated small systems only 4 to 7% have monitored for MTBE as reported to DHS. Thus, the general absence of MTBE monitoring data for wells in small systems prevent the determination of both the actual frequency of MTBE impacts, as well as the potential risk posed by the contaminant to small water supplies. DHS has noted that many small water systems tend to be located in

outlying rural areas and draw their water from shallow aquifers (6). Shallow aquifer wells that are designated as particularly vulnerable by DHS (within 2000 feet of a gasoline UST, refinery, or pipeline) may be at significantly higher risk for MTBE contamination.

Complete benzene and MTBE sampling frequency by size of water system, classification of system and regulating agency is given in Appendix 3-A.

MTBE Impacts to Public Drinking Water Wells. Among the drinking water wells monitored to date, the occurrence of MTBE impacts has been limited. As of March 1998, a total of 2,297 public drinking water wells have been tested for MTBE; 19 wells report MTBE detections, and 8 of these have exceeded the lower limit of $20 \mu\text{g L}^{-1}$ recommended in the 1997 US EPA Drinking Water Advisory (Table 3.2). In an additional 4 cases MTBE data for wells with known MTBE impacts was absent from the database (3 Santa Monica wells and 1 Tahoe well). Maximum MTBE concentrations greater than the California Draft Health Advisory Level of $35 \mu\text{g L}^{-1}$ have resulted in closure of municipal groundwater supplies in Santa Monica and in temporary closure in Marysville.

In Santa Monica, two separate aquifers, containing a total of 7 wells in the Charnock and Arcadia well fields, are impacted by MTBE and have been closed. These two aquifers supplied approximately 49 percent of Santa Monica's drinking water. The City of Santa Monica has an average daily water demand of 13.6 million gallons. Thus, the local impact to regional groundwater resources for the Santa Monica water supply is clearly significant. In addition, the South Tahoe Public Utility District has had 3 wells impacted by MTBE below regulatory action levels and has chosen to close these wells as well as 4 additional wells potentially threatened by MTBE/BTEX plumes from LUFT sites (11).

Comparison of MTBE and Benzene Impacts. To coarsely examine MTBE and benzene impacts to drinking water, we have compared the overall frequency of MTBE detections above action levels of 20 to benzene impacts above $1 \mu\text{g L}^{-1}$. Testing for benzene has been required under "regulated chemical" status since February 1989. As of March 1998, maximum concentrations of benzene above the Californian MCL of $1 \mu\text{g L}^{-1}$ were reported for 0.42 percent of the active public wells tested (36 out of 8,613 wells). Limited MTBE testing began in 1995 and early 1996, with the vast majority of MTBE monitoring occurring from late 1996 to the present. A total of 2,297 active wells have been monitored for MTBE as reported to DHS. Of these, 10 wells (0.44%) had detectable concentrations above the official $5 \mu\text{g L}^{-1}$ detection limit for purposes of reporting set by DHS. Maximum detected concentrations exceeding the lower limit of US EPA recommended levels of $20 \mu\text{g L}^{-1}$ were reported for 8 wells (0.35 percent of public wells tested). Therefore, testing of active public drinking water wells is limited as compared to benzene monitoring, however, the overall frequency of detections above current action levels are similar.

Table 3.2.. MTBE detections in California groundwater sources as reported by DHS as of March 1998

System Name	Well Name	Maximum MTBE Concentration ($\mu\text{g L}^{-1}$)
Santa Monica-City, Water Division	Charnock Well 18 - Inactive	31
	Charnock Well 13 - Inactive	130
	Charnock Well 19 - Inactive	300
	Charnock Well 16 - Inactive	NA*
	Charnock Well 15 - Inactive	NA*
	Arcadia Well 05 - Inactive	72
	Arcadia Well 04 - Inactive	NA*
Marysville, Cal-Water Service Co.	Well 03-01	115**
Presidio of San Francisco	Well 06 - Abandoned	23
	Well 13 - Abandoned	500
Los Angeles-City, Dept. of Water & Power	Tujunga Well 05	0.5
	Tujunga Well 04	1.8
	Verdugo Well 01	0.8
	Verdugo Well 02	13***
	North Hollywood Well 17	3.5
San Bernardino City	19 th Street	11
Cal. State Polytechnic Univ.- Pomona	Well 01	2.8
City of Sebastopol	Well 04	0.25
South Tahoe PUD	Tata Well 04	26
	Arrowhead Well 01	NA*
	Arrowhead Well 02	1.8
Calleguas Municipal Water District	Fairview ASR Well	0.6
Jurupa Community SD	Well 11 - Standby	0.7

* NA = Not available; reports of MTBE detections are absent from the DHS database.

** Eight samples taken in June 1997 indicate consistent concentrations of approximately $20 \mu\text{g L}^{-1}$.

***Multiple samples taken over a period of seven months indicate typical concentrations of approximately $2.5 \mu\text{g L}^{-1}$.

To directly compare occurrence of MTBE and benzene in the same population of wells, we examined the frequency of impacts at current regulatory levels among the 2,297 wells tested for MTBE. Eight wells among this set (0.35 percent) had MTBE impacts. Benzene impacts were reported for 14 wells (0.61 percent). Surprisingly, in all cases where wells were impacted with either MTBE or benzene, simultaneous detection of both compounds above regulatory action levels was never reported.

These results suggest that as of March 1998, MTBE impacts to drinking water wells were similar to benzene impacts given current regulatory action levels. However, in California gasoline formulations have changed significantly; use of wintertime Oxyfuels began in 1992 and year-round use of Reformulated Gasoline began in 1996. It is possible that most MTBE impacts to drinking wells to date may have occurred from gasoline releases pre-dating the use of MTBE in the large volumes (~11%) present in current gasoline formulations. If many of the occurrences of MTBE in drinking water wells are due to pre-1992 gasoline releases, then current frequencies of MTBE versus benzene impacts will not likely be predictive of future impacts. Increased monitoring, further

characterization and/or remediation of leaking UST sites in close proximity to active drinking water supply wells may be necessary to avoid unacceptable risk because, at present, it is not possible to accurately predict to what extent MTBE in shallow groundwater at the many leaking underground storage sites in California will affect deeper aquifers.

3.3. MTBE Detections in Private Drinking Water Wells

According to a 1990 census, there are 464,621 private drinking water wells in California. Private wells are regulated by individual counties and monitoring for organic chemicals is not required by law. Therefore, benzene and MTBE data from private wells is not available and the potential hazard from MTBE cannot be quantified. Because private wells typically pump shallow groundwater, these wells may be at greatest risk of MTBE contamination from the large number of LUFT sites throughout California, which are sources of MTBE in shallow groundwater.

3.4. Acknowledgments

We thank Paul Collins, Dr. David Storm and Duncan Wilson of the California Department of Health Services for providing us with current DHS data, contained in WQM and PICME databases.

3.5. References

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3.6. Appendix

Table 3-A. Sampling Frequency by system size, system classification and regulatory agency.

(1)			Benzene		MTBE	
	Systems with active groundwater sources	Active sources in these systems	% of these systems tested	% of these sources tested	% of these systems tested	% of these sources tested
All Systems						
community	2640	8994	64.6	69.8	16.6	24.8
non-transient, non-community	978	1244	35.1	33.8	2.1	2.1
non-community	2407	2713	14.5	13.5	0.2	0.3
state small	150	160	20.0	20.0	1.3	1.3
total	6175	13111	39.3	54.1	7.5	17.3
All Large Systems						
community	878	6544	88.7	78.6	42.6	32.7
non-transient, non-community	6	33	66.7	78.8	0.0	0.0
non-community	11	16	9.1	12.5	9.1	18.8
state small	0	0	NA	NA	NA	NA
total	895	6593	87.6	78.5	41.9	32.5
All Small Systems						
community	1762	2450	52.6	46.3	3.6	3.8
non-transient, non-community	972	1211	34.9	32.6	2.2	2.1
non-community	2396	2697	14.5	13.5	0.2	0.1
state small	150	160	20.0	20.0	1.3	1.3
total	5280	6518	16.6	14.1	1.7	1.9

(2)			Benzene		MTBE	
	Systems with active groundwater sources	Active sources in these systems	% of these systems tested	% of these sources tested	% of these systems tested	% of these sources tested
State Systems						
community	1558	7596	78.5	75.7	26.8	29.0
non-transient, non-community	408	564	44.6	43.4	3.9	3.7
non-community	926	1055	12.2	11.8	0.2	0.4
state small	56	61	5.4	4.9	3.6	3.3
total	2948	9276	51.6	66.0	14.8	24.0
Large State Systems						
community	871	6508	88.9	78.7	42.7	32.7
non-transient, non-community	4	27	75.0	81.5	0.0	0.0
non-community	5	9	20.0	22.2	20.0	33.3
state small	0	0	NA	NA	NA	NA
total	880	6544	88.4	78.6	42.4	32.5
Small State Systems						
community	687	1088	65.4	58.0	6.6	6.9
non-transient, non-community	404	537	44.3	41.5	4.0	3.9
non-community	921	1046	12.2	11.7	0.1	0.1
state small	56	61	5.4	4.9	3.6	3.3
total	2068	2732	35.9	35.8	3.1	3.6

(3)			Benzene		MTBE	
	Systems with active groundwater sources	Active sources in these systems	% of these systems tested	% of these sources tested	% of these systems tested	% of these sources tested
County Systems						
community	1058	1345	43.9	36.4	1.5	1.3
non-transient, non-community	561	666	27.6	25.1	0.9	0.8
non-community	1452	1628	16.1	14.7	0.2	0.2
state small	90	93	30.0	31.2	0.0	0.0
total	3161	3732	27.8	24.8	0.8	0.7
Large County Systems						
community	4	10	50.0	20.0	25.0	20.0
non-transient, non-community	1	2	0.0	0.0	0.0	0.0
non-community	6	7	0.0	0.0	0.0	0.0
state small	0	0	NA	NA	NA	NA
total	11	19	18.2	10.5	9.1	10.5
Small County Systems						
community	1054	1335	43.8	36.5	1.4	1.1
non-transient, non-community	560	664	27.7	25.2	0.9	0.8
non-community	1446	1621	16.2	14.7	0.2	0.2
state small	90	93	30.0	31.2	0.0	0.0
total	3150	3713	27.9	24.8	0.7	0.6

Sampling Frequency for benzene and MTBE in California's Public Water Systems.

Only systems classified by DHS as active, containing groundwater sources classified as active are included. Results are presented for all systems, large systems (200 or greater service connections), and small systems (less than 200 service connections). Results for each are grouped by system classification (community, non-transient non-community, non-community, and state-small).

- (1) All systems and corresponding sources as described above.
- (2) State regulated systems and corresponding sources as described above.
- (3) County regulated systems and corresponding sources as described above.

Testing and reporting requirements are summarized in the text (sec 3.3).

Note: Some systems not classified as being either state or county regulated in DHS databases result in discrepancy between totals in (1) and those derived through summing results in (2) and (3).

4. MTBE Fate at California LUFT Sites

4.1. Distribution of MTBE and benzene at LUFT sites

We have further evaluated 1995/96 data for 236 California LUFT sites (described in Section 3) to examine the relationship between the occurrence and magnitude of MTBE and benzene detections in individual monitoring wells. The groundwater data for the vast majority of these sites consisted of analytical results for total petroleum hydrocarbons, benzene, and MTBE from one sampling of groundwater from the 1,858 individual monitoring wells in this population of sites. We examined the correlation between concentrations of TPH, benzene, and MTBE in individual wells. Among these parameters, benzene and TPH show the strongest correlation ($\rho = 0.71$); MTBE and TPH concentrations show extremely weak correlation ($\rho = 0.27$); and benzene and MTBE concentrations show essentially no apparent correlation ($\rho = 0.14$). These results demonstrate that marked differences in the distribution of MTBE and benzene occur in individual monitoring wells at LUFT sites and that benzene and TPH concentrations are not predictive of MTBE concentrations in a given monitoring well.

4.2. Analysis of MTBE and Benzene Plumes

To further investigate the distribution of fuel hydrocarbons at LUFT sites, we plotted dissolved TPH, benzene, and MTBE groundwater plumes for 63 of the 236 MTBE LUFT study sites. These sites had a minimum of eight sampled monitoring wells and reported analytical results for concentrations of both benzene and MTBE for one sampling event. Concentration contours for dissolved TPH, benzene, and MTBE plumes were plotted by hand using our best professional judgment in conjunction with SWRCB hydrogeologists. Contours were defined to 50, 1, and 20 $\mu\text{g L}^{-1}$ for TPH, benzene and MTBE, respectively. For each site, analytical data from groundwater in monitoring wells and estimates of average groundwater gradient directions were used to contour the groundwater plume and to estimate its spatial extent.

In agreement with the moderate correlation found between concentrations of benzene and TPH in individual monitoring wells, benzene plume contours generally co-located and often resembled the overall shape of TPH plume contours. In contrast, the overall shape and location of MTBE plumes showed greater variation.

4.3. MTBE and Benzene Plume Length

The distance from the contaminant source to a drinking water supply which may complete a pathway to a human receptor, such as a groundwater well or a surface water intake, can be used to initially estimate the level of risk posed to drinking water sources by contaminants present in shallow groundwater at LUFT sites. Presently in California, the State Water Resources Control Board (1) as well as a Regional Water Board (2), and a Local Oversight Program Agency (3), have proposed regulatory guidance for LUFT sites that use the distance between contaminant source and drinking water source as a

screening tool in schemes to prioritize LUFT sites as either “low or high risk” cases. We have estimated the length of MTBE and benzene plumes at LUFT sites to provide data for the foundation of this type of regulatory approach. In order to compare MTBE and benzene concentrations of similar regulatory significance, we measured benzene plumes at $1 \mu\text{g L}^{-1}$ which is the California maximum concentration limit (MCL), and MTBE plumes at $20 \mu\text{g L}^{-1}$ representing the lower concentration level considered in the U.S. EPA 1997 Drinking Water Advisory (4). Further, it is not possible to measure plume lengths for MTBE at comparable concentrations to benzene, because the minimum detection limit for the majority of MTBE analysis at these sites is greater than $1 \mu\text{g L}^{-1}$.

Among these 63 sites, data were insufficient to define the benzene and/or MTBE plume lengths at approximately 20 percent of the sites. In the case of benzene, 12 sites lacked downgradient monitoring wells to delineate the benzene plume lengths and one site had a dissipated benzene plume ($< 0.5 \mu\text{g L}^{-1}$). Thirteen sites lacked information to define MTBE plume length for two reasons. First, in many cases detection limits for MTBE were very high due to dilution of samples prior to analysis for BTEX concentrations. Second, monitoring wells installed to define benzene plumes in some cases failed to delineate MTBE plumes, because the location and extent of the two plumes varied significantly.

Available data were sufficient to estimate the length for a total of 50 benzene and 50 MTBE plumes, while coincident plume lengths for both benzene and MTBE could be determined for 43 sites. Among this dataset, in 1995/96, 90% of MTBE plumes at $20 \mu\text{g L}^{-1}$ concentrations extended less than approximately 325 ft, while 90% of the benzene plumes at $1 \mu\text{g L}^{-1}$ measured less than approximately 400 ft (Figure 4.1). The results of this study agree well with other investigations that also reported typical benzene plume lengths of less than several hundred feet (5, 6, 7).

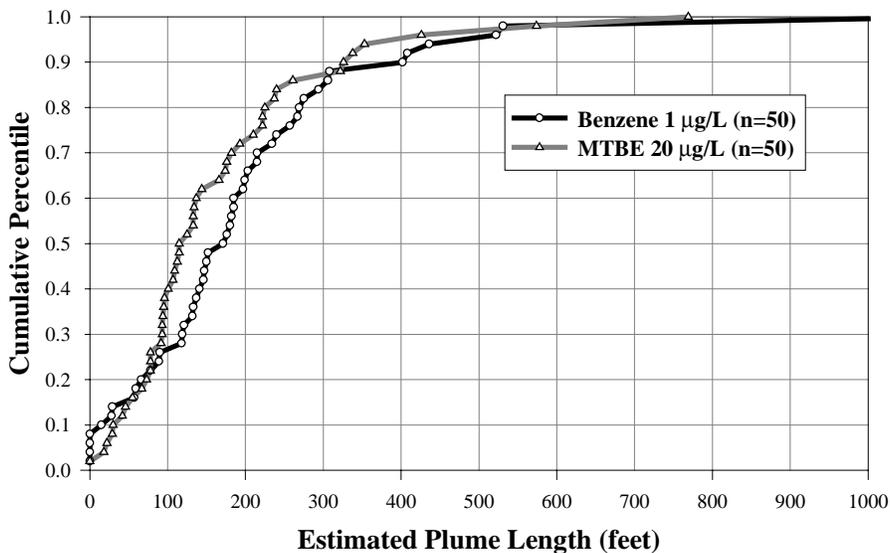


Figure 4.1. Cumulative distributions of 1995/96 plume lengths for benzene and MTBE.

We also compared MTBE and benzene plume lengths on a site-by-site basis to determine the degree of MTBE migration relative to that of benzene at individual LUFT sites (Figure 4.2). Because there are inherent uncertainties in estimating plume lengths, we compared the relative percent difference between MTBE and benzene plume lengths. A relative percent difference of greater than 50 percent was chosen as being indicative of significant differences. The majority (81 percent) of MTBE plumes in this dataset ($20 \mu\text{g L}^{-1}$ contour) were nearly equivalent or shorter than the corresponding benzene plumes ($1 \mu\text{g L}^{-1}$) at a given LUFT site (Figure 4.2) based on a relative percent difference of MTBE to benzene plume length of less than +50%.

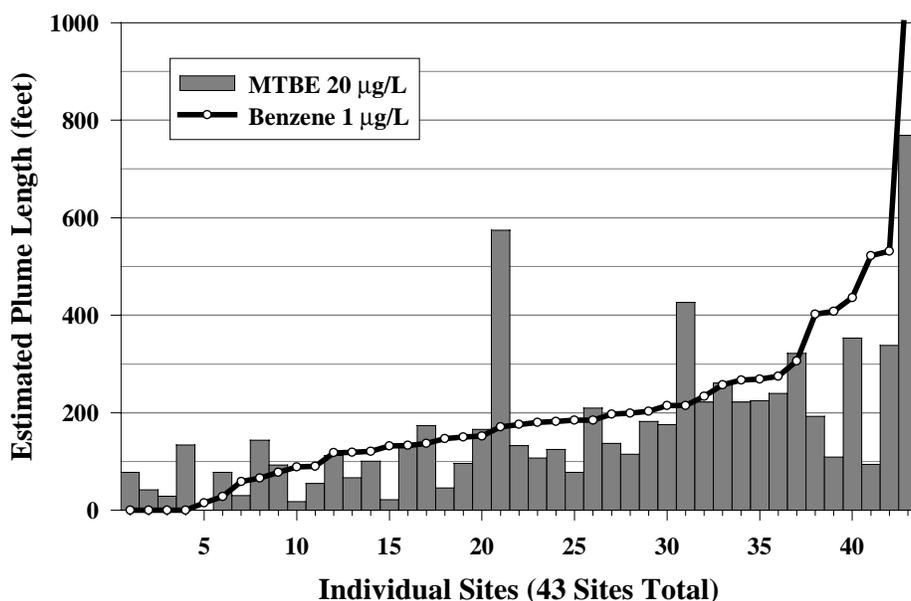


Figure 4.2. Comparison of 1995/96 MTBE and benzene plume lengths at 43 individual LUFT sites.

4.4. Correlation of Benzene and MTBE Plume Lengths

To test whether the length of benzene plumes is predictive of the length of MTBE plumes at individual LUFT sites, we calculated correlation coefficients between estimated lengths and between the rank of estimated lengths for 43 plume study sites where both MTBE and benzene plume lengths could be defined. The correlation coefficient between benzene plume lengths at $1 \mu\text{g L}^{-1}$ and the corresponding MTBE plume lengths at $20 \mu\text{g L}^{-1}$ is 0.73. Rank correlation is similar with a correlation coefficient of 0.73. These results indicate that there exists a moderate linear relationship between benzene and MTBE plume lengths. This moderate correlation is assumed to be the result of equivalent controlling variables such as groundwater velocity and source strength. Therefore, at a given site, the length of the benzene plume is moderately predictive of the potential MTBE impact, but this relationship contains significant variability. For example, the ratio of MTBE to benzene plume lengths at individual LUFT sites ($20 \mu\text{g L}^{-1}$ and $1 \mu\text{g L}^{-1}$ contours, respectively) varied from 0.18 to 3.4.

4.5. Discussion

Given both the predicted high mobility and high recalcitrance of MTBE in the subsurface, these results appear to contradict expected MTBE behavior. For example, assuming a single coincident release scenario, the resulting MTBE plume is expected to migrate further from the release point than the benzene plume due to preferential retardation and biodegradation of benzene. This behavior has been demonstrated *in situ* for a controlled single point release at the Borden Aquifer Site (8). Therefore, several factors need to be considered when interpreting 1995/96 plume length results. First, the release history may be the most important factor in determining the relative degree of migration of MTBE versus benzene at a LUFT site since multiple and/or chronic long-term releases of gasoline with and without MTBE may have occurred. For example, recent releases of petroleum hydrocarbons containing significant quantities of MTBE may have occurred at sites that in the past were impacted by gasoline containing little or no MTBE and higher concentrations of benzene. Therefore, the “release dates” for MTBE and benzene are not likely the same at the majority of LUFT sites. Second, while the vast majority of benzene plumes are apparently stable (5, 6, 7), it remains to be evaluated whether the majority of MTBE plumes are stable or transient. If the majority of MTBE plumes have not reached steady state yet (possibly due to the relatively recent releases of petroleum hydrocarbons containing large quantities of MTBE), results obtained from 1995/96 plume length data may not be indicative of future plume lengths. Third, we have evaluated plume lengths based on regulatory action levels of 1 µg/L for benzene and 20 µg/L for MTBE; obviously, lower regulatory action levels for MTBE (for example, the 14 µg/L limit being considered by the California Department of Health Services) may result in significantly different relationships between MTBE and benzene plume lengths.

Plume lengths inferred from 1995/96 data provided the first available information concerning the spatial extent of dissolved MTBE plumes for a population of LUFT sites given the current monitoring well networks at these sites. These results suggest that the dissolved benzene groundwater plumes measured during 1995/96 were of larger regulatory concern in 1995/96 than the respective MTBE plumes at the majority of LUFT sites analyzed in this study.

These results should not be interpreted such that MTBE plumes are always thought to be shorter than those of benzene. On the contrary, at least 20% of them appear to be significantly longer based on current action levels. In addition, extremely long MTBE plumes have been reported throughout the United States. For example, at Port Hueneme, California, a 2,500-meter long MTBE plume has been characterized (9). This plume is growing at approximately one foot per day. Long plumes are likely to be observed if the free product source has high fractions of MTBE and local groundwater velocity is great. These conditions may not be typical in California because pre-1992 tank upgrades may have prevented many high concentration MTBE releases and extreme groundwater velocities are by definition uncommon. We expect to see a great deal of variability with respect to the severity of MTBE impacts. Attention given to small to moderate impacts should in no way be used to minimize the significance of the minority of sites expected to

have the most severe impacts. Conversely, the existence of serious MTBE plumes does not imply that all MTBE releases will result in significant impacts relative to those of benzene.

4.6. Acknowledgment

The authors gratefully acknowledge the work of California SWRCB staff and students, Leo Savalin, Annette Cornelius, Raul Barba, and Sushma Dutta, for researching LUFT site data, performing database entry, and plotting plumes. We thank Kevin Capone for producing site maps.

4.7 References

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5. San Diego County Leaking Underground Fuel Tank Sites: Analyses of MTBE and Hydrocarbon Impacts

5.1. Background

The use of methyl *tert*-butyl ether (MTBE) as the preferred oxygenate in California Reformulated Gasoline has raised concerns relating to contamination of groundwater resources. MTBE has been detected at approximately 75% of California leaking underground fuel tank (LUFT) sites previously studied by Lawrence Livermore National Laboratory. Furthermore, at 70% of these sites concentrations exceed the limit of $14 \mu\text{g L}^{-1}$ proposed by the state Office of Environmental Health Hazard Assessment. Because MTBE is highly soluble in water and thought to be recalcitrant, it presents a management problem that differs significantly from that of the aromatic hydrocarbons (BTEX). To address this issue we are collecting and analyzing time series data from LUFT sites throughout California made available by request from major petroleum distributors. Here we present results of statistical analyses of time series data from 29 sites, located in San Diego County, with uniquely extensive MTBE time-series data. Comparisons are made between observed MTBE, BTEX and TPH concentrations. Parallel analysis of BTEX and MTBE plume characteristics is presented for comparison of known and potential impacts resulting from historical releases of the non-conservative aromatic hydrocarbons and relatively recent releases of the potentially recalcitrant contaminant MTBE.

5.2. Introduction

MTBE is a particularly difficult contaminant to study based on field data. While studying aromatic hydrocarbons (*e.g.*, benzene, toluene, ethylbenzene, xylene; or collectively, BTEX) is already difficult, assessing the environmental fate and transport of MTBE at LUFT sites is even more challenging. This is due to a variety of reasons including (a) limited existing monitoring networks, (b) multiple sources of on-site variability (hydrogeological heterogeneity, infiltration, water level fluctuation, etc.), (c) historic MTBE-monitoring data that are extremely limited as compared to those of BTEX compounds, and, perhaps most important, the often unknown (d) extent and (e) history of releases. In the case of BTEX compounds, monitoring at most LUFT sites has been ongoing for years, at some sites, more than a decade. Although MTBE has been used in gasoline as an additive for nearly twenty years, monitoring for its presence at LUFT sites has been required only since August 1996 after concerns were raised over contamination of drinking water aquifers in Santa Monica, California (1). As a result, at most LUFT sites throughout California, sufficient data for even the simplest statistical and time series analysis is just now becoming available. As this data is accumulated, organized and analyzed, much will be learned regarding the extent of MTBE contamination of groundwater and its associated risks. Past analyses have been based largely on detailed field studies (2,3), and limited available field data from real world LUFT sites (4-6). The focus of this study is to investigate existing field data in order to gain insight into how BTEX and MTBE behave at LUFT sites.

Here, the purpose is to analyze field data from 29 sites located in San Diego County. Data spanning a time period from early 1992 to late 1996 was submitted voluntarily by a major petroleum company to Lawrence Livermore National Laboratory (LLNL). More recent data have not yet been submitted to this study. MTBE data prior to 1995 are extremely rare and the time series data for the San Diego sites is significantly more extensive than what is currently available for the majority of California's LUFT sites.

It should be understood that this work is a hazard analysis focused on quantifying the occurrence and extent of MTBE impacts at LUFT sites relative to hydrocarbons. The work presented here addresses MTBE impact in terms of its threat to water resources. A complete treatment of the risk associated with MTBE pollution is fundamentally dependent on quantifying exposure and likely consequences to human health as well as understanding its impact on the beneficial use of water resources. Fully addressing the human health issue will require both exposure assessment and toxicity data that are not available at this time. Because there is no consensus on the toxicity of MTBE, human health risk will likely remain uncertain for some time into the future.

To assess the magnitude of MTBE impacts to groundwater, several simple statistical inquiries are presented. Rather than focusing exclusively on MTBE, MTBE contamination is compared to that of hydrocarbons, specifically BTEX and total petroleum hydrocarbons (TPH). Thus, the differences between these substances are emphasized; it is these differences that have raised the greatest concerns with respect to MTBE. In particular, relative to the aromatic hydrocarbons, MTBE is known to have a much greater affinity for water and, consequently, is significantly more soluble and mobile in groundwater. In addition, whereas the aromatics biodegrade in the environment, MTBE is believed to be recalcitrant or at best resistant to biodegradation. These characteristics suggest that MTBE, relative to the aromatic hydrocarbons, has the potential to occur at higher concentrations in groundwater, travel further from leak sources, and potentially present a cumulative contamination hazard which is not an issue for easily degraded compounds.

5.3. Results

5.3.1. Site Representativeness

The goal of the MTBE project at LLNL is the assessment of MTBE in groundwater at point source releases throughout California. Given that the present work is limited to 29 sites in a single county, one cannot assume that this population is fully representative of the majority of LUFT sites throughout the state. Previous work suggests that MTBE may be found at approximately 75% of LUFT sites impacting groundwater in California (see chapter 3). There are presently 32,409 LUFT sites recognized in the state; 13,278 at which hydrocarbons are known to have impacted groundwater (7). A best-case estimate of the number of MTBE impacted sites in California is approximately 10,000. An additional 2,915 and 16,216 LUFT sites are classified as having unknown impacts to groundwater and as soil-only impacts, respectively. In addition, an unknown number of sites have yet to be investigated and as a result remain unaccounted for. These sites may be significant because in the absence of site investigation it is unlikely that tank upgrades or other leak prevention strategies have been implemented. Thus, the above estimate

may be overly optimistic. The sites in this study represent, at most, approximately 0.3% of the total MTBE-impacted LUFT sites in California. In addition, these sites are located in a limited geographical subsection of the state. Therefore, it is important to consider how representative this population of sites is relative to the statewide population.

Crude statistical analyses of site hydrogeology, contaminant impact and similar details suggests that the site population used in this study, although limited, may be reasonably representative of the state of California. First, we have compared the proportions of all California LUFT sites within various geologic settings to those of the San Diego County set. Second, we compared depth to groundwater data and groundwater elevation ranges of the 29 study sites to a population of 236 MTBE sites that had been investigated previously by our group, and to all sites in the LLNL LUFT database for which sufficient data existed (1217 sites from the LLNL 1995 Historical Case Analyses, (HCA) (8)). Third, the number of wells at these sites was used as an indicator of the extent of site characterization and fourth, maximum measured concentrations of TPH, benzene and MTBE were used to estimate and compare impact severity between site populations.

The geologic setting of California LUFT sites was established by locating sites on a geological map of the state (9) using geographical information system (GIS) software. For the San Diego sites, bore logs were also examined to confirm consistency between mapped units and local formation data. Statewide, the majority of LUFT sites (~80%) reside on alluvial deposits characterized by layers of clays, silts, sands, and gravels. Approximately 5% of sites are located on loose to moderately consolidated sandstone, shale, and/or gravel deposits (conglomerate), 2% are found on granite, and 2% on pyroclastic volcanics (10). Of the 29 MTBE sites, 12 are located on alluvium, 10 on moderately consolidate conglomerate, 6 on granite and 1 on pyroclastic volcanics. These differences appeared less significant on inspection of site-specific bore logs. The logs suggested that the vast majority of these sites, 25, occur on sediments typical of alluvial deposits; three of these contained significant conglomerate material. Only three sites indicated significant granite in the bore logs, two under approximately ten feet of sediments, and one was almost entirely granite. One site is exclusively volcanic. In summary, 85% of the sites are found in geologic settings that are typical of the vast majority of California LUFT sites (loose to moderately consolidated sediments). The remaining 15% are located in less typical but representative settings (granitic and volcanic rock).

We compared statistics of the number of wells per site (Table 5.1), average depth to groundwater by site, and maximum range in groundwater elevation by site (Table 5.2). The degree of characterization based on the quantity of wells at individual sites was similar for all site populations. The average number of wells per site is approximately 9 with a standard deviation of approximately 6. For average depth to groundwater the 1995/96 MTBE data was only available for 29 of 236 sites. Historical data for 193 of these sites was available through the LLNL LUFT HCA database; this more extensive data set was used for comparison because, in contrast to the former, it represented multiple sampling events. Analysis of all data sets yielded an average depth to groundwater of approximately 23 feet with a standard deviation of about 20 feet. The average of maximum range in groundwater level was approximately 11.5 feet with a

standard deviation of 12.6 feet for the LLNL LUFT HCA set and approximately 8 feet for the MTBE data sets.

Table 5.1. Population size, mean and standard deviation for the number of monitoring wells at LUFT sites for various site populations. Mean values are given with 95% confidence intervals.

Data Set	Sites	Mean	St. Dev.
San Diego County	29	10.62 ± 2.31	6.30
LLNL HCA	1217	9.44 ± 0.34	6.10
SWRCB	236	8.30 ± 0.73	5.40

Table 5.2. Population size, mean and standard deviation for depth to groundwater and maximum groundwater elevation range at LUFT sites for various site populations. Mean values are given with 95% confidence intervals.

Data Set	Sites	Depth to Groundwater (feet)		Maximum Groundwater Elevation Range (feet)	
		Mean	St. Dev.	Mean	St. Dev.
San Diego County	29	20.16 ± 6.15	16.89	10.43 ± 2.89	7.94
LLNL HCA	1186	23.53 ± 1.21	21.23	11.58 ± 0.72	12.61
SWRCB	193	23.42 ± 2.55	18.09	11.81 ± 1.22	8.57

Site maximum concentrations of TPH, benzene and MTBE for the three data sets are shown as cumulative distributions (Figure 5.1). For TPH and benzene, the obtained distributions were very similar for the LLNL LUFT HCA set and the San Diego County set. Benzene data were in particularly strong accordance, whereas TPH data had an equivalent median value with slightly less variability (steeper curve) in the San Diego County data set. Concentrations for both TPH and benzene were generally lower in the 1995/96 MTBE data set. This trend reflects the limited number of sampling events rather than true concentration differences. The 1995/96 data set was based on a single sampling round at each site whereas maximum concentrations identified in the other data sets often occurred within a period of several years over many sampling rounds. This phenomenon also makes it difficult to judge the significance of results obtained by comparing maximum MTBE concentrations among the two available data sets. Values for the San Diego County data set are significantly higher than are those of the 1995/96 data set. It is not certain how much of this shift was due to greater MTBE impacts in the San Diego County set and how much was due to the effect of comparing time-limited and time-extensive sampling histories; as discussed later, the latter may have been relatively more important.

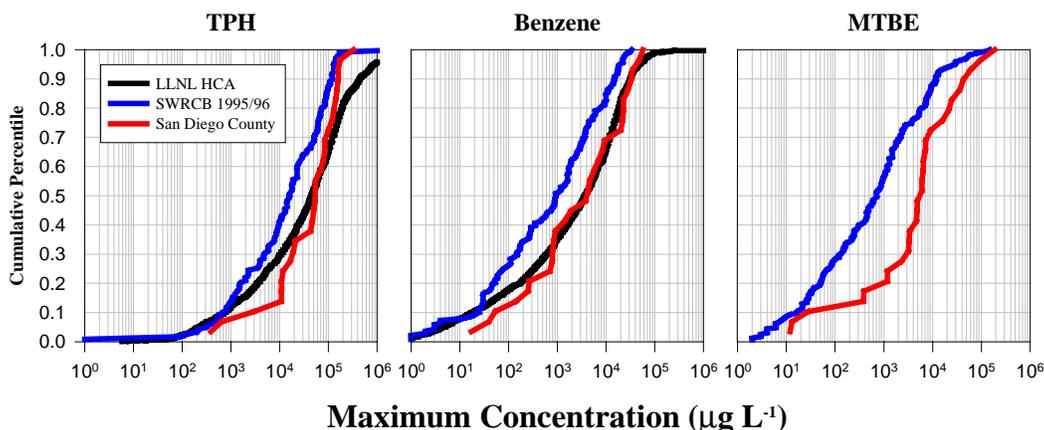


Figure 5.1. Comparison of maximum concentrations. Cumulative distributions of maximum TPH, benzene, and MTBE concentration for comparison between site populations. Sites from the SWRCB 1995/96 population for which no MTBE was detected were excluded from the MTBE curve.

In summary, the San Diego County sites appeared to be similar in many ways to site populations known to be more representative of the state of California. We cannot know for certain if trends observed from this set of sites will be replicated throughout the state but it may be likely. An important missing piece of information in the comparison of these data sets is the distribution of groundwater velocity, which is the most significant parameter controlling the transport of MTBE. Hydraulic conductivity, needed for velocity estimation, is measured at very few LUFT sites. Thus, comparison is not currently possible. If groundwater velocities at the San Diego County sites differ significantly from those of the statewide population, results of the following analyses may be biased.

5.3.2. Approach

We have focused on statistical analyses of a population of sites, rather than analysis of individual cases to identify general trends in the behavior of MTBE, TPH and BTEX contaminant plumes. Rather than examining MTBE plume behavior in isolation, we compared it to that of hydrocarbon plumes to reduce variability and place MTBE in context.

The San Diego County data set contained MTBE sampling data over the five-year period between 1/1/92 and 12/31/96. However, early data were sparse and for many sites nonexistent. Therefore, our analyses typically focused on the four-year period between 1/1/93 and 12/31/96. Sampling results were only included when coincidental data for TPH, BTEX and MTBE were available. The data set consisted of 29 sites, 327 wells and 5436 samples, of which 2320 were coincidental. Analyses followed five lines of inquiry.

1. Are the ranges of MTBE concentrations similar to BTEX concentrations among a population of LUFT sites? At an individual site is the concentration of MTBE similar to the BTEX or TPH concentrations?

The statistical nature of the magnitude of groundwater impacts was estimated and compared between MTBE and BTEX for both the entire population and between individual sites. First, cumulative distributions of site average and site maximum concentration were constructed to compare the magnitude MTBE and BTEX impacts on a population-wide basis. Second, correlations between average and maximum MTBE and BTEX concentrations at individual sites were calculated.

Average and maximum concentrations observed among a population of individual sites are shown as cumulative distributions (Figure 5.2). The shape of all concentration curves was similar, indicating similar statistical distributions. Maximum concentrations were generally an order of magnitude greater than average concentrations. TPH was significantly shifted towards higher concentrations, approximately two orders of magnitude for low concentrations and up to one order of magnitude for high concentrations. MTBE concentration values tended to bound those of the BTEX compounds.

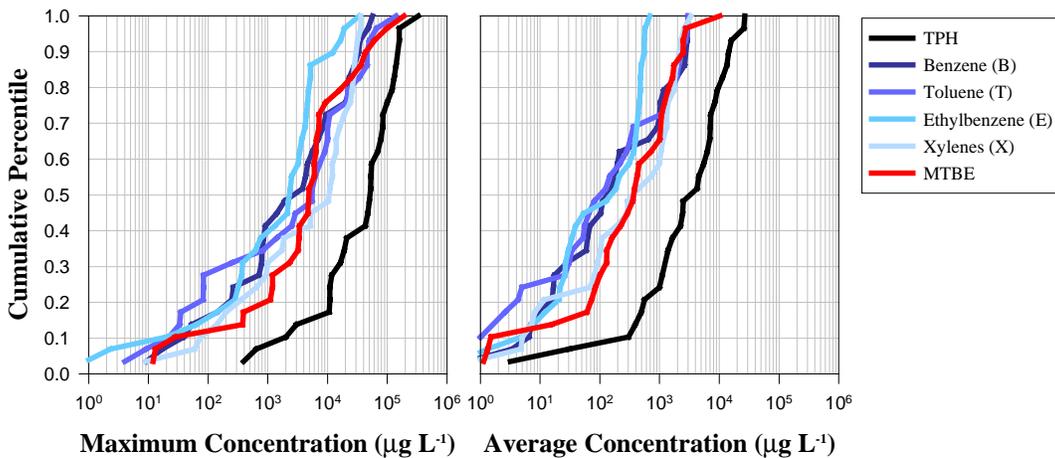


Figure 5.2. Cumulative distributions of maximum and average concentrations of TPH, BTEX and MTBE observed at individual sites.

Site average and maximum concentrations of MTBE on a population-wide basis were not found to be vastly larger than those of the BTEX compounds. To see if this relationship existed at individual sites within the population we examined how these values correlated on a site-by-site basis (Table 5.3). Significant correlations were observed between TPH and BTEX species; correlation coefficients ranged from 0.62 to 0.91 and 0.71 to 0.89 for average and maximum values, respectively. In clear contrast, average and maximum concentrations of MTBE are entirely uncorrelated with those of hydrocarbons; correlation coefficient values ranged from -0.06 to 0.08 and -0.08 to 0.09 for average and maximum

values, respectively. Results were generally improved for log average and log maximum concentrations. In these cases, an existent but poor correlation between MTBE and hydrocarbons was identified, with correlation coefficients ranging from 0.36 to 0.54 and 0.25 to 0.33 for maximum and average concentration, respectively. These results demonstrate that knowledge of the levels of any BTEX species or TPH at a site is largely predictive of the severity of impact for all BTEX compounds, but cannot be used to predict MTBE impact. The severity of MTBE impact at a site is highly variable with respect to BTEX and TPH.

Table 5.3. Intra-site average and maximum concentration correlation coefficients (29 sites) between total petroleum hydrocarbons (TPH), benzene (B), toluene (T), ethylbenzene (E), xylenes (X), and MTBE.

Average Concentration Correlation							Maximum Concentration Correlation						
	TPH	B	T	E	X	MTBE		TPH	B	T	E	X	MTBE
TPH	1.00						TPH	1.00					
B	0.74	1.00					B	0.85	1.00				
T	0.80	0.89	1.00				T	0.89	0.92	1.00			
E	0.79	0.73	0.76	1.00			E	0.77	0.71	0.82	1.00		
X	0.90	0.62	0.80	0.85	1.00		X	0.77	0.66	0.87	0.83	1.00	
MTBE	0.08	-0.02	-0.06	-0.01	0.05	1.00	MTBE	0.09	-0.07	-0.04	-0.08	-0.01	1.00
	Log TPH	Log B	Log T	Log E	Log X	Log MTBE		Log TPH	Log B	Log T	Log E	Log X	Log MTBE
Log TPH	1.00						Log TPH	1.00					
Log B	0.78	1.00					Log B	0.84	1.00				
Log T	0.73	0.81	1.00				Log T	0.90	0.91	1.00			
Log E	0.74	0.65	0.79	1.00			Log E	0.94	0.81	0.87	1.00		
Log X	0.74	0.76	0.92	0.91	1.00		Log X	0.91	0.79	0.92	0.91	1.00	
Log MTBE	0.25	0.29	0.33	0.26	0.30	1.00	Log MTBE	0.43	0.40	0.54	0.36	0.38	1.00

2. Are MTBE and BTEX spatially associated at LUFT sites? Does this association vary over time?

Occurrence and co-occurrence of MTBE and hydrocarbons was assessed by examining probabilities of detection and conditional probabilities of detection above threshold concentrations. Threshold concentrations were defined at 1000 µg L⁻¹, 1 µg L⁻¹, and 5 µg L⁻¹ for TPH, BTEX components and MTBE, respectively.

Overall probabilities of detection above threshold concentrations for the 2320 samples were calculated (Table 5.4). TPH concentrations above 1000 µg L⁻¹ were detected in 35% of all samples. Detections of BTEX components above 1 µg L⁻¹ were more frequent, occurring in 52%, 47%, 47%, and 49% of all samples for benzene, toluene, ethylbenzene, and total xylenes, respectively. Thus, the average detection probability for all BTEX compounds was approximately 50%. The probability for detecting MTBE above 5 µg L⁻¹ was 49%, essentially equivalent to the probabilities of BTEX detection. Therefore, MTBE was detected, above the given threshold values, with the same frequency as all BTEX components in this population of LUFT sites.

Table 5.4. Threshold concentrations and overall detection probabilities above threshold concentrations of total petroleum hydrocarbons, benzene, toluene, ethylbenzene, and total xylenes (2320 coincident sampling events over 327 wells).

Compound	Threshold Concentration ($\mu\text{g L}^{-1}$)	Total Detections Above Threshold Concentration	Probability of Detection Above Threshold
TPH	1000	812	0.35
Benzene	1	1198	0.52
Toluene	1	1082	0.47
Ethylbenzene	1	1093	0.47
Xylenes	1	1237	0.53
MTBE	5	1133	0.49

Table 5.5. Conditional probabilities of detection; Probability of detecting row analyte above threshold concentration given detection of column analyte above threshold concentration (2320 sampling events over 327 wells).

	TPH	B	T	E	X	MTBE
B	0.95		0.89	0.92	0.87	0.68
T	0.92	0.80		0.86	0.83	0.59
E	0.95	0.84	0.87		0.84	0.63
X	0.96	0.90	0.95	0.95		0.68
MTBE	0.71	0.65	0.62	0.65	0.62	

Conditional probabilities of detection are used to investigate co-occurrence of contaminants in individual monitoring wells. For example, given benzene detection above its threshold concentration in a monitoring well, we determined the corresponding probability of detecting MTBE at a concentration above its threshold (Table 5.5).

This analysis demonstrated that TPH and BTEX are highly associated; given detection of TPH above $1000 \mu\text{g L}^{-1}$, the probability of detecting each of the BTEX components was approximately 95%. MTBE was less often associated with TPH, with a conditional probability of 71%. Individual BTEX compounds were also commonly located in the same monitoring wells; conditional probabilities between BTEX compounds ranged from 80% to 95% with an average of 88%. This implies tight spatial agreement between benzene, toluene, ethylbenzene, and xylene plumes. Conditional probabilities of detecting MTBE above $5 \mu\text{g L}^{-1}$ given BTEX detection above $1 \mu\text{g L}^{-1}$ or of detecting BTEX given MTBE were similar, ranging from 59% to 68% with an average of 64% and 65%, respectively. Thus, although MTBE was detected with the same overall frequency as BTEX components, these contaminants often resided in different monitoring wells (~30-40% of the time). In other words, the spatial association between BTEX component plumes was demonstrably greater than that found between BTEX component plumes and those of MTBE.

The conditional probabilities were calculated on a quarterly basis to estimate spatial association over time between different contaminant plumes. The sampling frequency in 1993 was found to be relatively sparse and erratic so the three-year period from 1994 to 1996 was used for temporal analysis. Probabilities of detection decreased slightly over the sampling history for all species (Figure 5.3). The probability of MTBE detection behaved similarly to that of BTEX compounds except for the period from late 1995 to early 1996. During this period, the probability of MTBE detection dropped briefly before returning to the levels of the BTEX components. Thus, for the majority of the time series the probability of detection for MTBE and BTEX were similar.

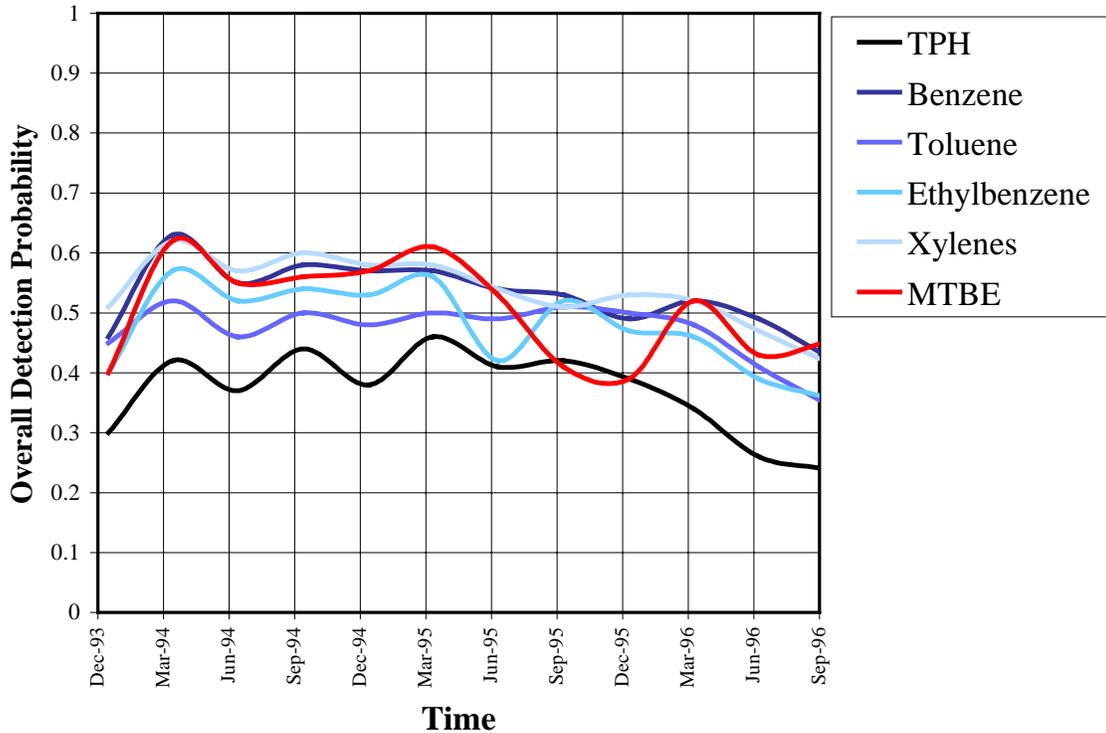


Figure 5.3. Overall probability of detection above threshold concentrations for TPH, benzene, toluene, ethylbenzene and total xylenes by quarter, 1/1/94-12/31/96.

Temporal conditional probabilities of detection (Figure 5.4) show that given the detection of a BTEX compound, the probabilities of detecting other BTEX components were consistent throughout time. MTBE behavior differed significantly; the conditional probability of detection of BTEX compounds given MTBE detection declined linearly over time by approximately 15-25%. This indicates an increasing dissociation of MTBE from BTEX plumes in the entire site population. Since the probability of co-occurrence of MTBE and BTEX decreased over time, the probability of MTBE occurrence unassociated with BTEX must have increased. Therefore, in some cases MTBE has moved from BTEX-impacted wells to BTEX-non-impacted wells. This implies a general dissociation of MTBE and BTEX plumes whereby MTBE is found beyond the margins of BTEX plumes with increasing frequency as time progresses.

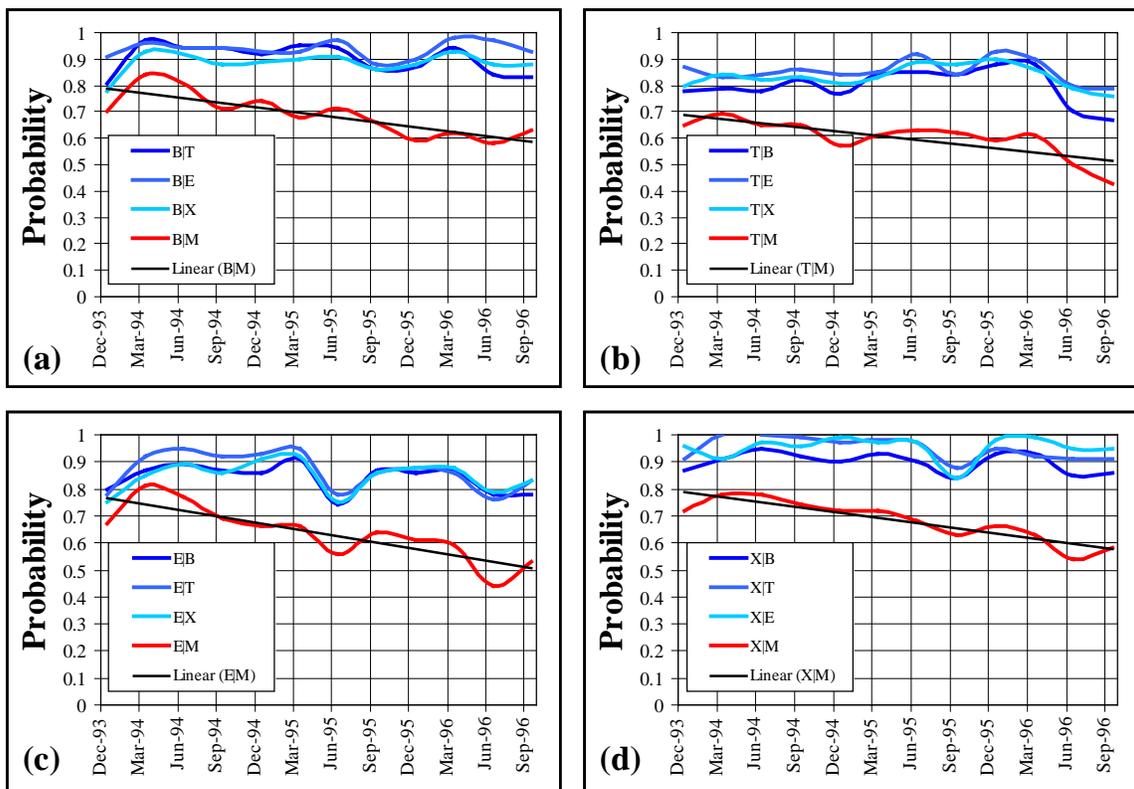


Figure 5.4. Conditional probabilities of detection of BTEX (benzene (a), toluene (b), ethylbenzene (c), and total xylenes (d)) given BTEX and MTBE detection by quarter, 1/1/94 - 12/31/96. (B|T = the probability of detecting benzene given the detection of toluene, etc.)

3. Are MTBE and benzene plumes influenced by hydrologic events?

We have examined whether mean MTBE and benzene concentration trends over the site population reflect significant changes in observed impact (generally increasing or decreasing concentration trends) or simply hydrological variation. MTBE and benzene concentrations in monitoring wells “near-the-source” (wells with large average TPH concentration, $> 1000 \mu\text{g L}^{-1}$) and wells “far-from-the-source” (wells with small average TPH concentration, $< 1000 \mu\text{g L}^{-1}$) were compared on a quarterly basis to changes in regional precipitation and average fluctuation of the water table.

Within the entire population of sites, mean concentrations appeared to be stable throughout the time history (no overall increasing or decreasing trends) (Figure 5.5) however, this does not indicate stability at individual sites. Most importantly spikes in MTBE and benzene concentrations are documented for both sets of wells. These spikes appear to be related to previous precipitation events. Fluctuation in the water table most certainly does influence concentration profiles; however, this effect was not clearly evident in the mean results but may be apparent on a site-by-site basis. Among near-source-area wells, surges in MTBE and benzene concentrations were approximately equal in magnitude, however, the mean MTBE concentration was approximately 5 to 6 times greater than that of benzene. Spikes in MTBE concentrations were especially pronounced for low TPH wells and deserve particular attention. In these wells, surges in MTBE concentrations were approximately one order of magnitude, significantly greater than surges in benzene concentrations. Thus, in wells outside of the source area, MTBE appears to be very responsive to hydrologic forcing. In addition, the highest MTBE concentrations may appear only briefly. As a result, low concentrations may be particularly deceptive during extended periods of drought.

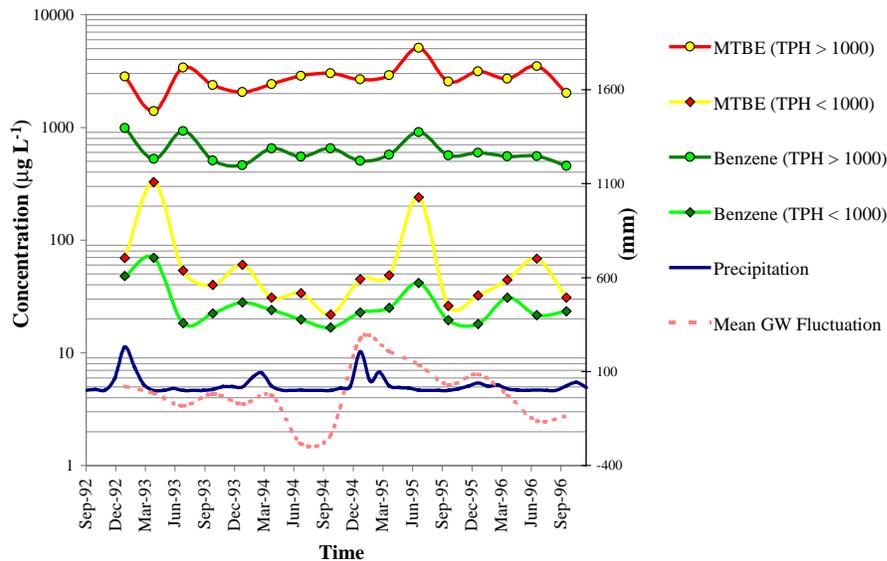


Figure 5.5. Geometric mean concentration for MTBE (M) and benzene (B) “inside” (TPH $> 1000 \mu\text{g L}^{-1}$) and “outside” (TPH $< 1000 \mu\text{g L}^{-1}$) of the high concentration TPH plume by quarter. Monthly precipitation, and mean deviation from average groundwater level are included for comparison.

4. How do levels of MTBE in downgradient wells compare with BTEX levels? What levels of MTBE and BTEX are traveling out of existing monitoring well networks?

Concentrations in downgradient wells are of significant practical importance. The severity of impact to these wells suggests the magnitude of contaminant concentrations leaving established monitoring networks and, consequently, the effectiveness of these networks for monitoring and management. Significant mass flux past the boundaries of the monitoring networks may indicate limited ability to assess downgradient impacts. For each site, we selected wells that bounded the average downgradient direction, with the minimum requirement of at least one downgradient well. This was possible for 24 of the 29 sites.

Correlations between MTBE, BTEX and TPH were calculated for the maximum and average concentrations found in downgradient wells (Table 5.5). Correlation was moderate to high among hydrocarbon compounds and poor to nonexistent between the hydrocarbons and MTBE. Correlations between MTBE and hydrocarbon compounds in the downgradient wells were improved but poor when using Log-transformed values of average and maximum concentrations. Therefore, while the impact of a given hydrocarbon species in a downgradient well was often reflective of that of the others, it was not related to magnitude of MTBE impact. This implies that the plume lengths of hydrocarbon components are significantly correlated with each other but not so much with that of MTBE. This agrees with our previous analysis of plume lengths from 1995/96 data from 63 California LUFT sites (see chapter 4).

Table 5.6. Downgradient concentration correlation; Intra-site average and maximum concentration correlation coefficients between total petroleum hydrocarbons (TPH), benzene (B), toluene (T), ethylbenzene (E), total xylenes (X), and MTBE in downgradient monitoring wells.

Average Concentration Correlations in Down Gradient Wells							Maximum Concentration Correlations in Down Gradient Wells						
	TPH	B	T	E	X	MTBE		TPH	B	T	E	X	MTBE
TPH	1.00						TPH	1.00					
B	0.92	1.00					B	0.93	1.00				
T	0.97	0.89	1.00				T	0.97	0.93	1.00			
E	0.65	0.50	0.56	1.00			E	0.94	0.79	0.91	1.00		
X	0.99	0.89	0.95	0.71	1.00		X	0.99	0.90	0.99	0.97	1.00	
MTBE	-0.04	-0.07	-0.07	0.06	-0.03	1.00	MTBE	-0.01	-0.02	-0.03	0.07	-0.01	1.00

Average Concentration Log-transformed Correlations in Down Gradient Wells							Maximum Concentration Log-transformed Correlations in Down Gradient Wells						
	Log TPH	Log B	Log T	Log E	Log X	Log MTBE		Log TPH	Log B	Log T	Log E	Log X	Log MTBE
Log TPH	1.00						Log TPH	1.00					
Log B	0.75	1.00					Log B	0.77	1.00				
Log T	0.76	0.88	1.00				Log T	0.72	0.84	1.00			
Log E	0.80	0.87	0.88	1.00			Log E	0.76	0.89	0.89	1.00		
Log X	0.76	0.84	0.95	0.95	1.00		Log X	0.72	0.86	0.91	0.96	1.00	
Log MTBE	0.49	0.32	0.25	0.40	0.27	1.00	Log MTBE	0.32	0.19	0.14	0.18	0.09	1.00

Levels of contaminant concentrations observed leaving the monitoring networks and the relationships between these levels on a site by site basis were evaluated by analysis of scatter plots of average and maximum concentrations of MTBE and BTEX as functions of average and maximum TPH concentration, respectively (Figure 5.6). Plots of average and maximum concentrations in downgradient wells are similar, with maximum values consistently an order of magnitude greater than average values. The most significant characteristic with respect to MTBE concentrations in the downgradient wells was that they were often significantly higher than BTEX concentrations and occasionally even higher than were those of TPH. The one-to-one curve for MTBE and BTEX concentrations versus TPH values is included for clarity. BTEX concentrations varied from several times lower to beyond two orders of magnitude lower compared to those of TPH. In contrast, MTBE concentrations showed no significant linear trend relative to TPH concentrations. For this group of sites, in terms of average concentrations in downgradient wells, 46% had average MTBE concentrations significantly greater than average BTEX concentrations by up to several orders of magnitude; 33% had average MTBE concentrations near the upper range of average BTEX concentrations; and 20% had significantly smaller average MTBE concentrations relative to those of BTEX. Results for maximum concentrations in downgradient wells were similar.

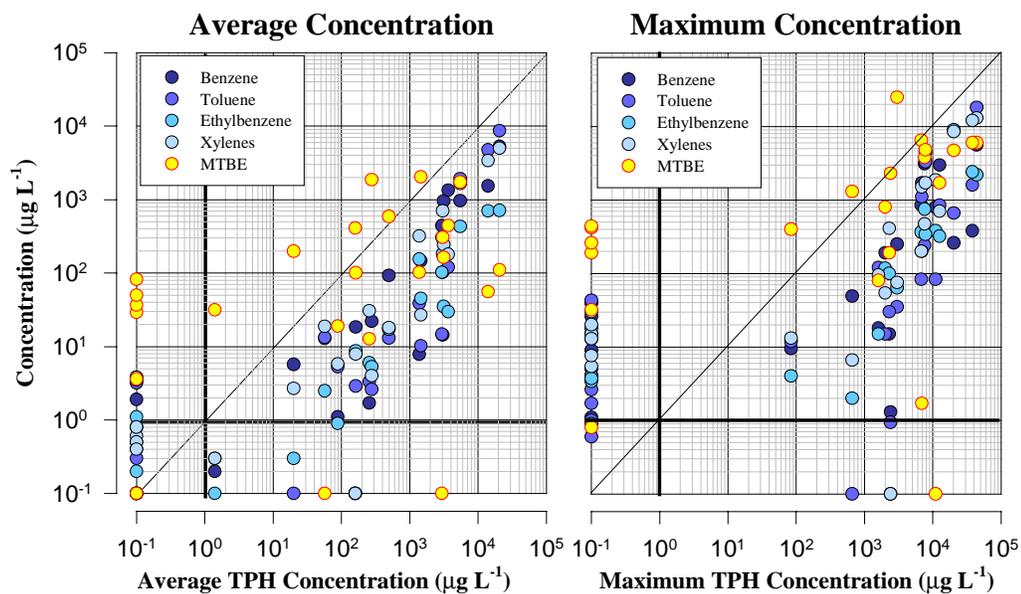


Figure 5.6. Average and maximum concentrations of MTBE and BTEX versus TPH in downgradient wells by site (values on axes are > 0.0 and $< 0.1 \mu\text{g L}^{-1}$).

5. Can attenuation of MTBE or benzene be demonstrated in our existing monitoring networks?

Attenuation of MTBE relative to benzene is a primary concern. Benzene is known to biodegrade in a variety of field settings while the studies to date indicate no significant intrinsic biodegradation of MTBE (Chapter 6). Therefore, attenuation of MTBE at LUFT sites may be dominated by or restricted to dispersion of the contaminant following dissolution. If this scenario is true, one would expect relatively small reductions in MTBE concentrations relative to benzene over an equivalent distance in the downgradient direction. To test this hypothesis, a near-source and a downgradient well were selected for each site. The near-source well was defined as the well having the greatest historical hydrocarbon impact (greatest average TPH concentration) and the downgradient well was defined as that downgradient well showing the greatest historical hydrocarbon impact. In cases where no downgradient well displayed measurable TPH concentrations, BTEX was used as a surrogate measure of hydrocarbon impact. Average concentrations of MTBE and benzene in the near-source wells are plotted versus the corresponding average concentrations in the downgradient wells (Figure 5.7). The reduction in concentration between the near-source well and the downgradient well is used to assess the attenuation capacity of MTBE relative to that of benzene.

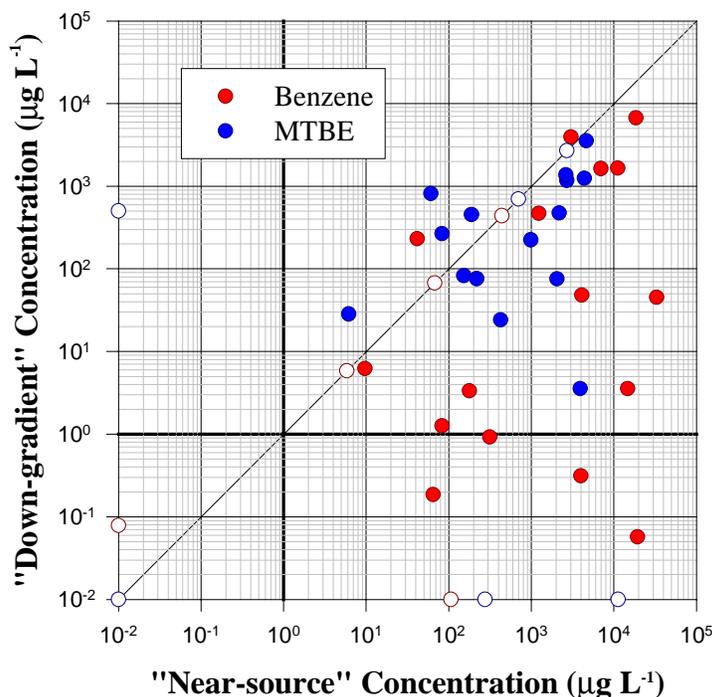


Figure 5.7. Average concentration of MTBE and benzene in the most highly TPH-impacted downgradient well vs. the most highly impacted well (“Near-source”). Open symbols represent concentrations at sites where both wells were identical or where contaminants were not detected (values on the axes are non-detect).

Only twenty-one out of the 29 sites were initially selected for this analysis. This was due to 3 sites with no appropriate near-source-well, and 5 sites at which no appropriate downgradient well existed. Several of the remaining sites were not considered useful for estimating attenuation (values shown as open symbols in figure 5.7). For some sites compounds were not detected in both wells and therefore were of limited value in gauging relative attenuation. At an additional three of the sites, average concentrations were identical in both wells. In these cases, the most severely impacted well was also found to be a downgradient boundary well.

Of the remaining sites, the majority (13 of 14 at which both wells could be defined and had observed MTBE detections) had average MTBE concentrations in the downgradient wells clustered near 0.1 to 10 times the average concentrations found in the near-source wells. At one site, the average concentration of MTBE in the downgradient well was significantly lower than that found in the near-source well (4 versus 4000 $\mu\text{g L}^{-1}$). In contrast, given the above constraints, 9 of 15 sites showed significant attenuation of average benzene concentrations (reductions between the near-source and downgradient wells of nearly 100 to 100,000 times). In other words, based on average concentrations, MTBE rarely showed significant attenuation potential relative to benzene, for which it was not universal, but common.

There are two important shortcomings implicit in these results. First, attenuation, as estimated, is a function of adequacy of the monitoring network configuration. For example, at three sites, the most impacted well was also a downgradient well. At these sites, as well as those where separation distances were small relative to the extent of the plumes, instrumentation may have been inadequate to resolve significant reductions in concentrations. Therefore, attenuation was sometimes unobservable but not necessarily absent. This generally appeared to be the case for MTBE plumes and much less so for benzene plumes. Additionally, benzene plumes may have been old relative to MTBE plumes. Therefore, benzene plumes were assumed to be somewhat stable. So if significant attenuation was observed it was likely to be actual. However, some of the MTBE plumes may have been recent and, therefore, still evolving. In these cases, observed attenuation may have reflected a situation where too little time had passed for the plume to become established at the downgradient well location. Nonetheless, despite these shortcomings, benzene clearly appeared to have the capacity to attenuate significantly over on-site distances with average concentrations dropping several orders of magnitude between the near-source and the downgradient well. This capacity appeared to be essentially absent for MTBE. Assuming equivalent dispersion, this difference can be attributed to preferential biodegradation of benzene.

These results are suggestive but are limited in that only data from two wells at each of 15 sites are employed. Further evidence of preferential attenuation of BTEX compounds was found through examination of the entire dataset using relative concentrations (Figure 5.8). Benzene detections were grouped by magnitude (*e.g.*, 1-10 $\mu\text{g L}^{-1}$, 10-100 $\mu\text{g L}^{-1}$, etc.) and for each group cumulative distributions of the concentration ratios between benzene and MTBE, toluene, ethylbenzene, or xylenes in individual monitoring wells were generated for coincident detections.

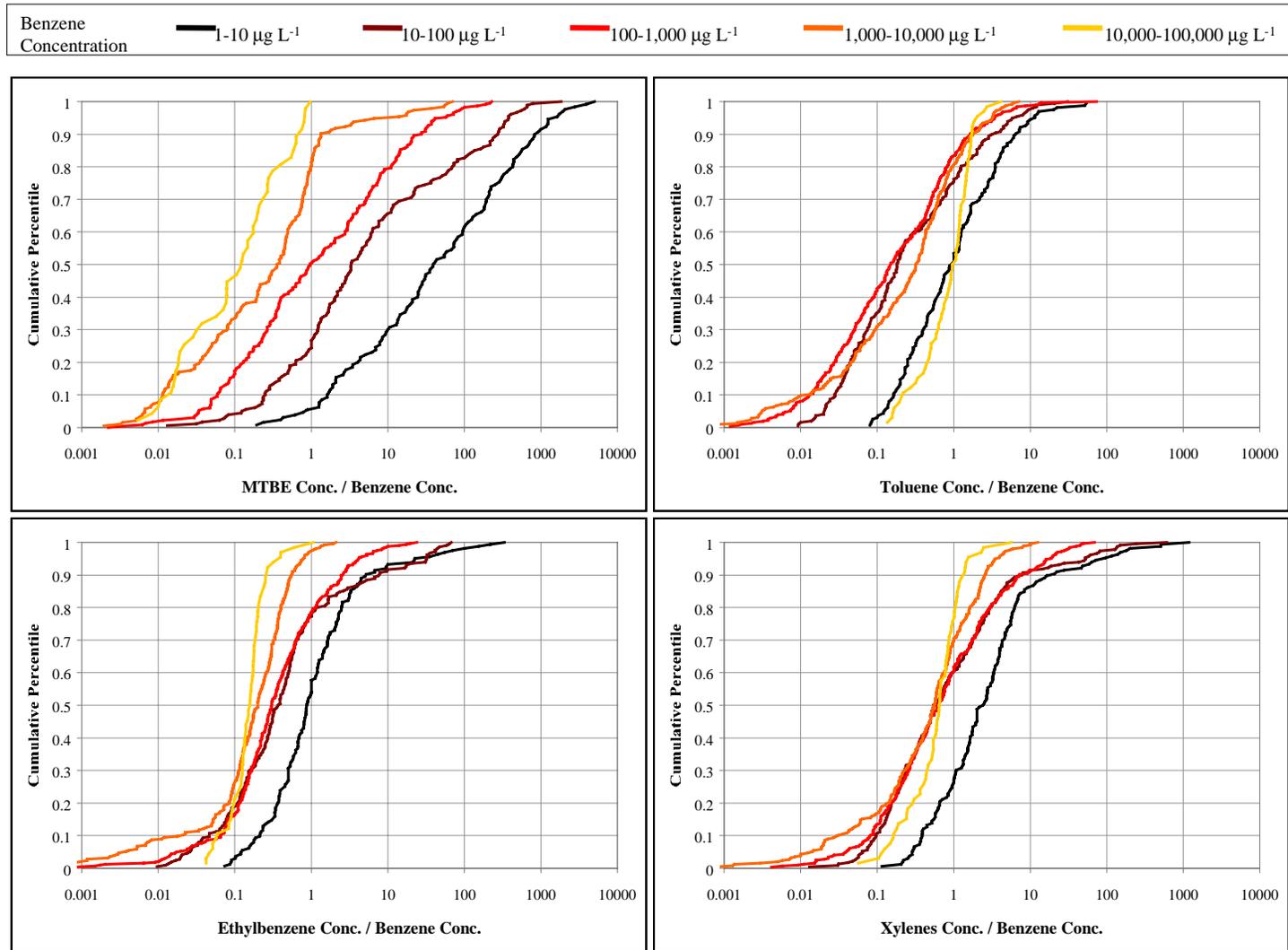


Figure 5.8 Cumulative distributions of the relative concentration ratios of MTBE, toluene, ethylbenzene and xylenes to benzene over various ranges of benzene concentration.

Given compounds with similar characteristics, the cumulative distributions of concentration ratios are expected to be similar regardless of the concentration range grouping because the compounds should attenuate in unison. This was evident in the ratio distributions of toluene to benzene, ethylbenzene to benzene, and xylenes to benzene. In each case, as the magnitude of benzene concentration changed, the distributions of the concentration ratios of the other BTEX compounds to benzene shifted by generally no greater than one order of magnitude. In other words, the magnitude of the relative concentrations was not strongly affected by the magnitude of the benzene concentrations. Therefore, as benzene concentrations decreased, the concentrations of toluene, ethylbenzene and xylenes decreased similarly. The noticeable differences in these curves are attributable to relatively small variations between the properties of the individual BTEX compounds.

MTBE behaved quite differently than toluene, ethylbenzene and xylenes when compared to benzene in this way. For high benzene concentrations ($10,000-100,000 \mu\text{g L}^{-1}$), the concentration ratio of MTBE to benzene ranged from 0.001 to a maximum of approximately 1. Therefore, for high benzene concentrations, MTBE concentrations were equivalent to or less than the corresponding benzene values. As benzene concentrations decreased, the cumulative distributions were shifted towards higher relative concentrations. For low benzene concentrations ($1-10 \mu\text{g L}^{-1}$), the relative concentration of MTBE to benzene ranged from approximately 1 to 1000. Therefore, when benzene concentrations were low, MTBE concentrations were at least equivalent and often much greater than those of benzene. This is clear evidence that as benzene concentrations were attenuated, MTBE concentrations relative to those of benzene increased dramatically. Therefore, MTBE has far less potential for attenuation than benzene and the other similarly behaved BTEX compounds.

5.4 Discussion

Several key pieces of information with respect to MTBE and the aromatic hydrocarbons are without doubt. First, MTBE is more soluble than BTEX compounds. Therefore, MTBE may occur at higher concentrations in groundwater. Second, hydrocarbons have a stronger affinity for organic material and will adsorb to organic carbon in soils more readily than MTBE. Therefore, MTBE is expected to be relatively more mobile than BTEX compounds. Combining the influence of higher concentration and greater mobility leads to the expectation that MTBE plumes will move further and faster than BTEX plumes. Third, aromatic hydrocarbons are known to be biodegraded by microorganisms commonly found in the subsurface. This and the presumed recalcitrance of MTBE is expected to augment the difference in the extent of MTBE and BTEX contaminant plumes. These hypotheses are simple, and assumed reliable given controlled circumstances.

However, such behavioral differences cannot be identified easily using extant LUFT site data. For example, source histories in terms of leakage rate and composition are generally unknown. Thus, for any given LUFT site it is difficult if not impossible to predict how the plume should behave based on dissolution considerations. In addition,

hydro- and hydrogeological parameters are spatially and temporally variable. As a result, it can be difficult if not impossible to predict the fate of a given plume with precision and confidence even if the source is well characterized. Given these limitations, this work has focused on general trends using simple statistical and graphical treatment of the data, rather than detailed analysis of individual sites.

The expectations regarding MTBE and BTEX plumes were generally supported by the analyses of this data set. Occurrence and co-occurrence analyses showed that BTEX and TPH plumes were strongly associated with each other; while association between BTEX and MTBE was significant but more limited. Most importantly, the degree of association between MTBE and BTEX plumes decreased significantly over time. Assuming that hydrocarbon plumes were generally “mature” (pseudo-steady-state), these results would indicate that MTBE plumes are still developing (transient) as a result of non-synchronous source histories.

The lack of association between hydrocarbon and MTBE plumes was further supported by statistics of site-specific average and maximum concentrations. These measures of impact showed significant correlation between the hydrocarbon species and the lack of correlation between the hydrocarbons and MTBE. Thus, hydrocarbon impact is a poor predictor of MTBE impact. Sites with minimal hydrocarbon impacts may have relatively significant MTBE contamination and vice versa.

The site concentration statistics showed that average and maximum MTBE concentrations were generally greater than or equal to those of BTEX. Based on solubility arguments, observed MTBE concentrations were still lower than expected. A possible clue was found upon inspection of tank upgrade dates. For 16 of the sites, tank upgrade dates have been confirmed. Of these, 31% occurred in 1993, 44% between 1985 and 1990, and 25% prior to 1985. Therefore, for all sites at which confirmation was possible, tanks were upgraded and the leaks presumably terminated at or before the time when MTBE was introduced in gasoline in large fractions as an oxygenate. Second, over a 3 to 4 year period, the mean concentrations of both benzene and MTBE were stable over the population. If the majority of sites in the population had post-1992 releases of oxygenated fuel, noticeably increasing mean concentrations should have resulted. In addition the probability of detection should have increased with time. Therefore, because these trends were not observed, oxygenate plumes were, on average, established within the monitoring networks. However, they were mobile relative to those of the hydrocarbons based on co-occurrence probability data. Thus, available evidence indicates that the observed contamination was due to MTBE releases at unknown but, presumably, smaller fractions (MTBE was previously used as an octane-enhancing additive).

Wells with low TPH impact showed particularly erratic fluctuations that were associated with hydrological variability, precipitation in particular. The short duration spikes seen in the record are of particular concern in that they suggest that extended observation of low concentrations can be misleading. Significantly higher concentrations may be observed when hydrological conditions change. Spikes were observed after the particularly wet winters of 1992/93 and 1994/95. This behavior may have been absent

during the drought of the middle to late eighties. Upon individual inspection of six of the most characterized sites this phenomenon was clearly evident in many wells, both near the source and downgradient (anecdotal information not presented in the result section). Therefore, actual contaminant concentration may be significantly underestimated when relying on limited temporal data. For this data set, this source of uncertainty was greatest in wells with limited hydrocarbon impacts. This may help to explain the elevated maximum concentrations in this data set as compared to the 236 sites in the 1995/96 data (see Figure 5.1). In particular it is the lower concentration values, which show greater elevation in the San Diego data set.

Analysis of average and maximum concentrations in downgradient wells was especially informative. Based on solubility, mobility and recalcitrance, it is expected that MTBE has the potential to travel far downgradient in comparison to hydrocarbons. This behavior was reflected by concentrations observed in downgradient wells. At only 5 of the 24 sites, average and maximum concentrations were significantly less than those of the BTEX compounds. In general, MTBE concentrations in the downgradient wells were equivalent to or significantly higher than BTEX concentrations. At 6 of 19 sites where TPH was detectable in the downgradient wells, average MTBE concentrations exceeded those of TPH. At 4 of 6 sites where TPH was not measurable in the downgradient wells, MTBE concentrations exceeded those of BTEX by one to two orders of magnitude.

The implication of this is that at many of these sites MTBE was leaving established monitoring networks at significantly higher concentrations than individual aromatic hydrocarbons. Judging from observed average and maximum concentrations in downgradient wells, it appeared that some of these sites were inadequately instrumented to define plumes. In the case of MTBE, this situation was more prevalent. In addition, just as site average and maximum concentrations showed poor correlations between MTBE and hydrocarbons, so did the equivalent measures in the downgradient wells. Thus, monitoring networks installed to capture hydrocarbon plumes were sometimes not sufficient for monitoring of MTBE plumes.

Elevated MTBE concentrations compared to those of BTEX in downgradient wells were expected based on relative solubilities. In addition, biodegradation of the aromatic hydrocarbons and the lack thereof with respect to MTBE were expected to exacerbate the differences. Even though a portion of the sites was poorly bounded, substantial attenuation of benzene was observable. Nine sites out of 16 (57%) where benzene was measurable in the near-source and the downgradient well, and where the wells were not identical, showed convincing evidence of rapid attenuation (defined here as an observed decrease in average concentration of greater than approximately two orders of magnitude in the downgradient direction). Only one site, representing 7%, showed an analogous MTBE observation. Assuming equivalent dispersion, negligible volatilization from the dissolved phase, and a longer release history of benzene, only biodegradation could explain this behavior. As expected, benzene showed convincing evidence of its potential to biodegrade and MTBE did not.

5.5. Conclusion

We have performed statistical analyses of the data from a population of 29 LUFT sites. Since monitoring of MTBE at gasoline impacted groundwater in California was required very recently (August 1996), most LUFT sites in California have less than six sampling events for MTBE over an eighteen month period. Therefore, temporal analysis of data from almost all California LUFT sites is severely constrained. In contrast, the 29 San Diego sites analyzed in this study have MTBE monitoring data spanning a time period from early 1992 to late 1996. Even analysis this relatively better data set cannot provide a complete understanding of the fate and transport of MTBE in shallow groundwater. Site data collected for regulatory compliance typically are insufficient for segregating individual mechanisms and aspects of contaminant transport; both the uncontrolled release conditions and a lack of precise, accurate, and relevant measurements preclude this option. Admitting the limitations of available data, we have used statistical analyses of this data to identify significant trends in MTBE and BTEX behavior. Our analysis of MTBE and hydrocarbon contamination at 29 sites in San Diego County provides suggestive and compelling evidence in accordance with several expectations. First, that MTBE relative to BTEX components should occur at higher concentrations and show greater mobility, and second, that MTBE was expected to be recalcitrant and not likely to undergo the rapid attenuation seen for biodegradable BTEX compounds.

This is our first analysis of temporal data for MTBE plumes from a population of regulated LUFT sites. Of critical importance is, first, representativeness of these sites with respect to LUFT sites throughout the state, and, second, the implications of these results with respect to water resources. It is important to know if extrapolation of these results to the thousands of sites statewide is appropriate. It is also important to consider precisely what these results mean in a practical context if they do prove to be representative.

The available information on site characteristics was incomplete. Available information suggested that the San Diego County sites were similar compared to California LUFT sites in general. However, significant sources of bias may have existed. These sites were submitted for analysis by a single industry source and, therefore, the product released may not have been representative of the variability in blending composition existing between manufacturers. Additionally, in all cases where confirmation was possible, tanks were upgraded early so releases were likely representative of pre-oxygenate formulations. If this is the case, recent and future releases will eventually result in more serious impacts. In other words, what is currently observed at LUFT sites in California may often not be fully representative of the potential impact resulting from the recent use of MTBE as a fuel oxygenate.

Chosen regulatory action levels have a strong impact on the outcome of groundwater vulnerability analysis. Clearly, if the acceptable level for MTBE concentrations in groundwater was established several orders of magnitude higher than that of benzene, the MTBE problem would be considered minimal. However, based on the uncertainty involved in determining MTBE related health risk, the low taste and odor thresholds of MTBE, and public perception considerations, this is extremely unlikely. Probable

regulatory limits will be between ~14 to 20 $\mu\text{g L}^{-1}$ (or less) relative to 1 $\mu\text{g L}^{-1}$ for benzene. Since relative concentrations of MTBE to BTEX in downgradient wells are often expected to exceed 20 to 1, MTBE is likely to replace benzene as the regulatory benchmark at many sites.

Assuming regulatory levels of 1 and 20 $\mu\text{g L}^{-1}$ for benzene and MTBE, respectively, a crude estimation of relative magnitude of impact may be made. At 30% of these sites average MTBE concentrations in the downgradient wells exceeded 20 times the corresponding average benzene concentrations. Therefore, MTBE impacts must be considered more significant than those of benzene at a minority of these LUFT sites. However, this minority may be representative of several thousand sites throughout California. In addition, this estimation may be optimistic considering that given an initial concentration ratio of 1:20 (20 to 400 $\mu\text{g L}^{-1}$ for example), benzene is expected to attenuate to 1 $\mu\text{g L}^{-1}$ at a shorter distance than is required for MTBE to reach 20 $\mu\text{g L}^{-1}$ due to the preferential biodegradation of benzene.

In addition, management of MTBE is often expected to be difficult because instrumentation designed to monitor fuel hydrocarbon plumes was, in many cases, inappropriate for MTBE (sometimes even inappropriate for BTEX). In particular, these networks, based on the San Diego data set, were generally insufficient to demonstrate significant attenuation of MTBE. This may suggest an inadequacy of present monitoring networks for management of MTBE threats. More importantly, it is consistent with the hypothesis that MTBE is generally recalcitrant.

If this is true, consideration must be given to reformulating groundwater management paradigms. Management has generally focused on the local scale (individual sites). For management of compounds that are both ubiquitous and recalcitrant, the regional scale will become increasingly relevant. The reason that hydrocarbon impacts have not been more substantial, considering a long history of frequent releases, is primarily the result of biodegradation. In the absence of this removal mechanism contaminant accumulation in water systems needs to be considered. For example, assuming recalcitrance, a particular MTBE plume may eventually attenuate to acceptable concentrations due to dispersion but the mass is not depleted. The mass from multiple plumes may, therefore, contribute to regional degradation of entire groundwater basins. Groundwater basins in the most densely populated regions of the state are at the greatest risk. It is in these areas that the majority of LUFT sites are concentrated. In contrast to those of MTBE, the impacts of hydrocarbon (i.e. benzene) plumes are not often expected to extend beyond the local scale.

Assuming representativeness of these results, justification of continued use of MTBE as an oxygenate is considered fundamentally dependent on the establishment of sound regulatory limits for development of appropriate management strategies for both present and future impacts and the protection of both the beneficial uses of groundwater resources and human health. Setting limits is considered necessary for both the development of rational cost/benefit analyses and for the potential implementation of risk-based corrective action; both of which are likely to be important future issues. In

addition, clear demonstration that future leak prevention will be universally effective is required to minimize the risk of cumulative degradation of regional groundwater resources.

Now that more abundant data are becoming available, important future work will involve expansion of the data set. Ideally, several hundred sites distributed throughout the state will be analyzed over the next six months. This will greatly reduce uncertainty with respect to statewide representativeness.

5.6 References

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6. Examining *in Situ* Biodegradation of MTBE at Commercial LUFT Sites

6.1 Objective

We are examining the fate of a recalcitrant fuel oxygenate, methyl *tert*-butyl ether (MTBE), in the subsurface at leaking underground fuel tank (LUFT) sites. The LUFT sites in this study have been identified by the Santa Clara Valley Water District in conjunction with the San Francisco California Regional Water Quality Control Board as high risk sites, due to their proximity to public drinking water wells, and/or the presence of extremely high concentrations of MTBE in shallow groundwater. This project focuses on assessing whether intrinsic bioattenuation is occurring at these representative sites. This study is unique in that investigations at the selected LUFT sites are driven by regulatory concern. By further investigating these gasoline releases as field research sites, we are able to add depth and knowledge to compliance-driven investigations.

Recent studies have indicated that BTEX (benzene, toluene, ethylbenzene, and xylenes) plumes in groundwater are self-limiting in terms of length and growth rate as a result of biodegradation (1, 2, 3). The conclusions of these studies were based upon statistical analyses of plume lengths from a number of LUFT sites. These historical case analyses have exerted a significant impact on regulatory policies on a national level. While passive bioremediation can effectively remediate fuel hydrocarbon plumes, current studies show that MTBE is more mobile in the subsurface, and not biodegraded as easily as BTEX compounds. In addition, MTBE currently is considered a possible carcinogen. Clearly, establishing the potential for intrinsic biodegradation is essential for both deciding among remedial alternatives for treatment of MTBE-impacted sites and formulating corrective-action regulatory guidelines for fuel hydrocarbon plumes containing MTBE. We expect results from these investigations to have direct implications for LUFT sites throughout California and nation-wide.

6.2 Background

In contrast to benzene, MTBE (and other alkyl ether oxygenates) are difficult to biodegrade (4). Microcosm studies to date indicate an absence of intrinsic biodegradation of MTBE at the majority of LUFT sites. Several studies reported little to no biodegradation of MTBE under a variety of aerobic (5, 6) or anaerobic (denitrifying, sulfate-reducing, and methanogenic) (7, 8, 9) conditions using groundwater, landfill aquifer material, soils, and sludges as inoculum.

In a few cases, microcosm studies suggest that limited intrinsic biodegradation of MTBE may occur *in situ*. Sediments collected near the source area of a gasoline release in North Carolina showed slow and incomplete biodegradation (10). MTBE was degraded only in near source sediments under aerobic conditions after a 20-day lag period; initial concentrations were reduced from 2,100 to 1,000 - 1,500 $\mu\text{g L}^{-1}$ over a period of about 80 days, following which biodegradation ceased. Apparent evidence of aerobic degradation

of MTBE was also observed in groundwater microcosms from one of three wells at a Fuel Terminal Site in Sparks, Nevada (11). Concentrations of MTBE from 5,000 to 10,000 $\mu\text{g L}^{-1}$ were degraded after a 14-day lag at rates comparable to those of BTEX compounds. Incomplete aerobic biotransformation of MTBE was also suggested in a study using columns of sediment material from a USGS site in Trenton, New Jersey (12). After a lag period of 35 days, a decrease in 100 $\mu\text{g L}^{-1}$ MTBE concentrations, initially present at 100 $\mu\text{g L}^{-1}$, was correlated with increases in TBA concentration.

In the laboratory, MTBE biodegradation has been demonstrated for both mixed and pure bacterial cultures under aerobic conditions. These biodegradative cultures were enriched from activated sludges (petroleum refinery, municipal, and/or chemical plants) (13, 14) and from Ginkgo tree fruit (15). In addition, MTBE was shown to be cometabolically biodegraded by pure cultures of propane-oxidizing bacteria (16) and by a filamentous fungi (17). Successful enrichment of MTBE-biodegrading microorganisms has also been reported for granular activated carbon fluidized bed reactors (18) and a vapor phase compost-based biofilter (19).

During a controlled field experiment performed at the Borden aquifer in Ontario, Canada, MTBE-oxygenated gasoline was injected into shallow groundwater. Intensive sampling over 1.3 years demonstrated that MTBE was fully recalcitrant, exhibited no mass loss, while the mass of BTEX compounds was markedly reduced (20). After a lapse of 6 years, sampling resumed 240 meters downgradient where only a minor fraction of the originally introduced mass of MTBE was found. Interpretation of the later result indicates MTBE biodegradation is complicated by the absence of intermediate sampling time points and the presence of a landfill leachate plume in the predicted downgradient location of the MTBE plume. Therefore, it remains uncertain whether biodegradation contributed to the presumed loss of MTBE at this site.

6.3 Ongoing Activities

Commercial sites impacted by MTBE- and FHC-contamination are being tested for *in situ* biodegradation activity by integrating results from laboratory tests and field data. The overall goal is to obtain and analyze a complete dataset suitable for providing general conclusions concerning the fate of MTBE at LUFT sites. In this work, we are testing sediment and groundwater samples from a population of LUFT sites to elucidate general trends in the biodegradative behavior of MTBE, as compared to BTEX compounds. Further we are obtaining samples from a variety of redox zones to compare the potential for intrinsic biodegradation within aerobic and anaerobic areas of the plume.

Site assessment studies are being undertaken and paid for by industry partners. The majority of the field work proposed is required by regulatory agencies; however, additional data required solely for biodegradation studies is also included in the field work plan for site assessment. Therefore, data for research needs are being collected concurrently with data collected for compliance requirements.

In this ongoing study, soil and groundwater samples from the demonstration sites have been obtained during the site assessment investigations from temporary borings and borings for additional monitoring wells. The potential for MTBE biodegradation in soil and groundwater samples is being tested in laboratory microcosms under site-specific conditions. Microcosms are incubated under redox potentials, concentrations of dissolved oxygen conditions (*i.e.*, conditions ranging from aerobic to anaerobic), temperature, BTEX concentrations, and MTBE concentrations that mimic parameters defined during site assessment. Bioattenuation of other alkyl ether fuel oxygenates (*e.g.*, TAME) is also being examined if these are present at the site. Results from these studies will show the degradative potential of naturally occurring aquifer microorganisms for bioattenuation of MTBE at LUFT sites. If biodegradation of MTBE occurs in these sediments, we will quantify rates of *in situ* attenuation under both aerobic and anaerobic conditions, assess the long-term fate of MTBE degradation products in ground water, and test whether the presence of MTBE impacts the fate and biodegradation of BTEX and other FHCs.

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