

Evaluation of the Impact of Fuel Hydrocarbons and Oxygenates on Groundwater Resources

TOM SHIH,^{*,†,‡} YUE RONG,[‡]
THOMAS HARMON,[§] AND MEL SUFFET[†]

*Environmental Science and Engineering Program,
University of California at Los Angeles, 46-081 CHS,
Box 951771, Los Angeles, California 90095-1772,
Department of Civil and Environmental Engineering,
University of California at Los Angeles, 5732 G BH,
Box 951593, Los Angeles, California 90095-1593, and
California Environmental Protection Agency,
Regional Water Quality Control Board, 320 4th Street,
Suite 200, Los Angeles, California 90013*

The environmental behavior of fuel oxygenates (other than methyl *tert*-butyl ether [MTBE]) is poorly understood because few data have been systematically collected and analyzed. This study evaluated the potential for groundwater resource contamination by fuel hydrocarbons (FHCs) and oxygenates (e.g., *tert*-butyl alcohol [TBA], *tert*-amyl methyl ether [TAME], diisopropyl ether [DIPE], ethyl *tert*-butyl ether [ETBE], and MTBE) by examining their occurrence, distribution, and spatial extent in groundwater beneath leaking underground fuel tank (LUFT) facilities, focusing on data collected from over 7200 monitoring wells in 868 LUFT sites from the greater Los Angeles, CA, region. Excluding the composite measure total petroleum hydrocarbons as gasoline (TPH_G), TBA has the greatest site maximum (geometric mean) groundwater concentration among the study analytes; therefore, its presence needs to be confirmed at LUFT sites so that specific cleanup strategies can be developed. The alternative ether oxygenates (DIPE, TAME, and ETBE) are less likely to be detected in groundwater beneath LUFT facilities in the area of California studied and when detected are present at lower dissolved concentrations than MTBE, benzene, or TBA. Groundwater plume length was used as an initial indicator of the threat of contamination to drinking water resources. Approximately 500 LUFT sites were randomly selected and analyzed. The results demonstrate MTBE to pose the greatest problem, followed by TBA and benzene. The alternative ether oxygenates were relatively localized and indicated lesser potential for groundwater resource contamination. However, all indications suggest the alternative ether oxygenates would pose groundwater contamination threats similar to MTBE if their scale of usage is expanded. Plume length data suggest that in the absence of a completely new design and construction of the underground storage tank (UST) system, an effective

management strategy may involve placing greater emphasis on UST program for ensuring adequate enforcement and compliance with existing UST regulations.

1. Introduction

The production and use of fuel oxygenates, particularly methyl *tert*-butyl ether (MTBE), have increased dramatically since the early 1990s as a consequence to federal and state regulations designed to improve air quality. The 1990 Federal Clean Air Act (CAA) Amendments mandated the use of winter oxyfuel or reformulated gasoline (RFG) to reduce carbon monoxide or ozone-forming hydrocarbon emissions in carbon monoxide and ozone nonattainment regions, respectively (1). In theory, the federal oxyfuel and RFG requirements do not specify a particular oxygenate, and gasoline refiners have several oxygenate options, including ethers (e.g., MTBE, diisopropyl ether [DIPE], ethyl *tert*-butyl ether [ETBE], *tert*-amyl methyl ether [TAME]) and alcohols (e.g., ethanol or *tert*-butyl alcohol [TBA]). In practice, however, MTBE has emerged as the dominant oxygenate in oxyfuel and RFG due to its lower cost and favorable transfer and blending characteristics (2). Currently, MTBE accounts for 85% of all oxygenates used in the United States or roughly 15 billion L year⁻¹ (3). While ethanol accounts for about 7% of the United States oxygenated fuel supply, ethanol is generally not used outside of the Midwest (4).

Fuel oxygenates can be accidentally introduced to subsurface environments during the refining, distribution, and storage of oxygenated fuels. Spills and leaks of oxygenate-containing gasoline pose a greater risk to groundwater resources as compared to that caused by other petroleum constituents (e.g., monoaromatics such as benzene, toluene, ethylbenzene, and total xylenes [BTEX]). Comparing to other petroleum constituents, fuel oxygenates are significantly more water soluble and are not adsorbed as readily to soil particles (see Table S1, Supporting Information), allowing them to travel farther and faster in groundwater (4-6). In addition, owing in part to their molecular structure, ether oxygenates including MTBE have been shown to resist biodegradation (7-11). The persistence and mobility of MTBE in subsurface environment, combined with its relative quantity in oxyfuel and RFG as compared to other gasoline constituents, have contributed to its dominant presence and frequent detection in groundwater plumes (4) and community water systems (CWS) (12). The relatively low odor threshold of MTBE renders many of these drinking water supplies with even low-level MTBE contamination to be unusable (13).

Concerns about potential groundwater contamination from MTBE have led several states to consider or enact MTBE bans (4). Unless the oxygenate requirements are removed through modification of the CAA, state- and federal-level bans of MTBE mean refiners must replace MTBE with another oxygenate. As a result, interest in the use and the environmental fate and transport of alternative oxygenates has increased significantly (14). However, to date, the state of knowledge is still quite limited for oxygenates DIPE, ETBE, TAME, and TBA (which together make up a total of up to 8% of United States oxygenates market). There are virtually no data on the environmental behavior of these other oxygenates (15), due primarily to difficulties in delineating their extent in the environment, lack of systematic analytical procedures for their determination as a group, and lack of regulatory requirement for their analysis. The extent and magnitude of

* Corresponding author phone: (213) 576-6729; fax: (213) 576-6700; e-mail: Tshih@ucla.edu.

[†] Environmental Science and Engineering Program, University of California at Los Angeles.

[‡] California Environmental Protection Agency.

[§] Department of Civil and Environmental Engineering, University of California at Los Angeles.

oxygenate contamination (other than MTBE) in the United States remains unknown. It is imperative that the environmental impacts of alternative oxygenates be properly assessed, since limited evidence available suggests they would pose groundwater contamination threats similar to MTBE (4), if used in similar percent by volume amounts.

This paper characterizes the potential for groundwater contamination of fuel hydrocarbons (FHCs) and oxygenates by examining their occurrence, distribution, and extent at leaking underground fuel tank (LUFT) sites. Specifically, data on the frequency of detection, maximum concentration, and contaminant plume length in groundwater of FHCs and oxygenates at LUFT sites in the greater Los Angeles region are presented. Contaminant plume length is the primary measure in this research because it reflects the potential of the contaminant to impact receptors. Secondary analysis of the correlation among FHC and oxygenate plume lengths and concentrations and time series analysis of contaminant plume length are also presented. In addition, this paper addresses the role of fuel oxygenates in influencing the behavior of FHC plumes at LUFT sites. Analysis of these data provides information on the current extent/magnitude of impact to groundwater resources caused by fuel releases, addresses the fate and transport of released gasoline constituents, and provides a basis for making preliminary predictions on the implications of the expected shift to alternative oxygenates as MTBE is phased out, or reduced, in gasoline.

The approach utilized is to treat LUFT sites as statistical populations (1). LUFT sites are particularly important because they represent major point sources of gasoline constituents and the leading cause of FHC and oxygenate groundwater contamination. According to U.S. Environmental Protection Agency's (USEPA) Safe Drinking Water Information System, some 385 000 known releases of gasoline have already occurred at LUFT sites nationally (5) and approximately 35% of the CWS wells have one or more LUFT sites within a 1-km radius of the well (5). This paper focuses California, specifically the Los Angeles region, as California's large consumption of fuel oxygenates makes the state an important environmental indicator for the national impacts of oxygenates. In fact, California's consumption of MTBE accounts for approximately one-fourth of global MTBE consumption (4) and some 6700 MTBE LUFT sites are located within 0.8-km radius of CWS wells in the state (16). Los Angeles, which comprises about 28% of the population in California (17), exemplifies a typical RFG-program participating metropolitan area.

2. Experimental Section

2.1.1. Characterization of Contaminant Spatial Extent at LUFT Sites. Groundwater plume length for a given contaminant is defined as the distance from the source area to the farthest edge of the plume at a predetermined concentration contour. In this paper, the dissolved plume length in groundwater for FHC (benzene), oxygenates (MTBE, DIPE, ETBE, TAME, and TBA), and total petroleum hydrocarbons as gasoline (TPH_C) were investigated. TPH_C is a useful indicator of the presence and magnitude of gasoline contamination and includes C₄–C₁₂ compounds. Dissolved concentration contours were defined to 5 µg L⁻¹ for benzene and ether oxygenates to 10 µg L⁻¹ for TBA, and to 100 µg L⁻¹ for TPH_C, taking into account both uniformity across different analytes as well as their method detection limits (MDLs). For each site, analytical data from groundwater monitoring wells, estimates of average groundwater gradient directions, and best professional judgment in extrapolating the most down-gradient well contaminant concentrations to the respective predetermined concentration contours were used to contour the groundwater plume for estimating spatial extent. Other

investigators (1, 16, 18) have applied similar methods for characterizing plume length.

Clearly, plume length as defined is two-dimensional. The lack of depth-specific data and other site-specific knowledge across the population of LUFT sites investigated in this paper preclude evaluation of plume transport in the vertical direction. In areas of significant recharge, this can bias the measurements toward shorter plumes, since a typical monitoring well screened across the water table may fail to detect the leading edge of the plume as it is deflected downward in response to the infiltration of recharge from above. Further, fluctuating flow directions as well as errors in their determination can result in monitoring well network configurations that create additional biases in plume length measurement. Despite these shortcomings, plume length remains an important indicator of the spatial extent of solute plumes and, in this paper, reflects the potential/relative potential of the FHCs and oxygenates to impact receptors.

2.1.2. Site Selection and Sampling Protocol for Contaminant Plume Length Study. From a list of over 1100 active LUFT facilities in the greater Los Angeles region, 500 facilities were randomly selected for site evaluation. Facilities qualified for inclusion in the plume length study if (a) sufficient groundwater monitoring data were available to define the contaminant plume lengths, (b) groundwater monitoring data covered at least the time period from 3rd quarter 2000 to 2nd quarter 2001, (c) at least one of the five fuel oxygenates of interest (MTBE, TBA, DIPE, ETBE, and TAME) was used or detected at the site, (d) at least one of the FHCs (TPH_C and benzene) was used or detected at the site, and (e) site analytical data met California Regional Water Quality Control Board—Los Angeles Region's (CRWQCB-LA) laboratory quality assurance testing requirements (19).

To investigate the influence of oxygenates on FHC plume length at LUFT sites, a distinct "FHC-only" population of LUFT facilities was identified for comparison. From the same list of LUFT facilities referenced above, 700 facilities were randomly selected for site evaluation. The "FHC-only" population was selected based on identical facility inclusion criteria as above, with the exception that none of the five oxygenates of interest was used or detected at the site (as demonstrated by soil and groundwater historical data). For TPH_C and benzene, only for 53 and 52 facilities, respectively, were plume lengths able to be estimated after examination of all 700 randomly selected sites.

2.2. Occurrence and Distribution of FHCs and Oxygenates at LUFT Sites. To investigate the occurrence/distribution of FHCs and oxygenates, data from LUFT sites were analyzed to determine the frequency of detection of FHCs and oxygenates at LUFT sites, their maximum site concentrations, and the correlation among these gasoline constituents. As part of the recent regulatory requirements adopted by the California State Water Resources Control Board, responsible parties for LUFT sites were required to submit laboratory analytical data and reports to the state Geotracker Internet Database in the Electronic Deliverable Format (EDF). From a list of over 1100 active LUFT facilities in the greater Los Angeles region, over 850 facilities had submitted their laboratory analytical data and reports in EDF, which ensured the data that were transmitted were of known quality and met all laboratory testing requirements specified by the regulatory agency (section 2.4). The resulting EDF from these facilities uniformly analyzed, at a minimum, FHC (BTEX), oxygenates (MTBE, DIPE, ETBE, TAME, and TBA) and TPH_C. An extensive data analysis was conducted of the electronic data and hardcopy reports from these facilities. For the time period between January and March of 2002, a total of over 7200 monitoring wells were sampled for these facilities.

2.3. Site Setting and Representativeness. To determine whether the LUFT sites selected for this study were repre-

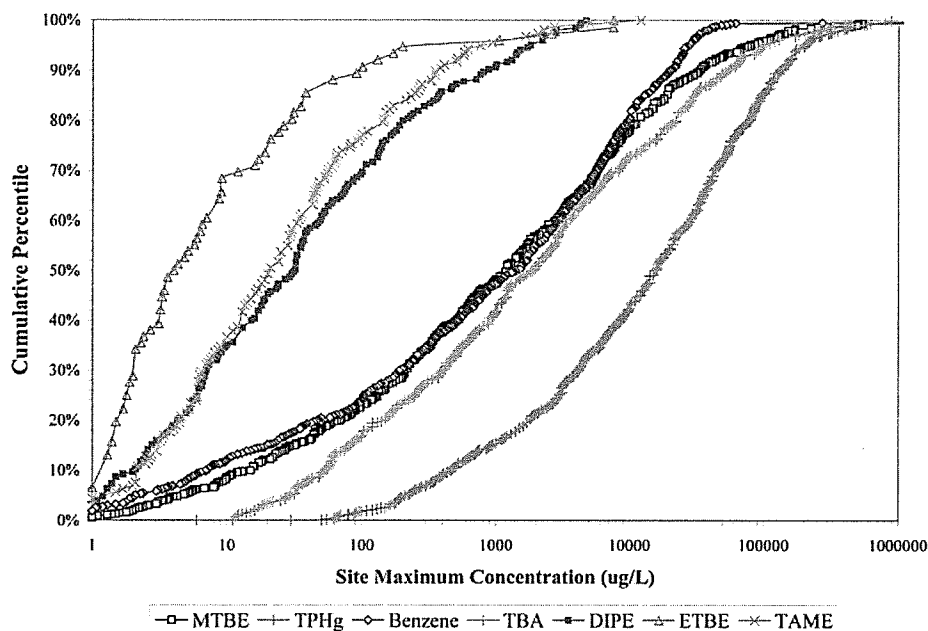


FIGURE 1. Plot of cumulative percentile of site maximum concentration for FHCs (TPH_c and benzene) and oxygenates (MTBE, TBA, DIPE, ETBE, and TAME).

TABLE 1. Summary Statistics on LUFT Site Maximum Analyte Concentrations and Site Analyte Detection Frequencies^a

	MTBE	TPH _c	benzene	DIPE	ETBE	TAME	TBA
minimum ($\mu\text{g L}^{-1}$)	0.46	30	0.3	0.36	0.35	0.38	6
maximum ($\mu\text{g L}^{-1}$)	1.6×10^7	9.98×10^8	4.2×10^7	4 700	7 500	12 000	4.4×10^6
median ($\mu\text{g L}^{-1}$)	1 200	15 000	1 370	30	4	20	1 880
mean ($\mu\text{g L}^{-1}$)	44 840	3 783 500	83 750	290	260	240	30 120
g-mean ($\mu\text{g L}^{-1}$)	900	11 400	700	31	7	24	1 730
LUFT sites with detected analyte (n)	718	797	716	206	77	159	530
analyte site detection frequency (%)	82.7	91.8	82.5	23.7	8.9	18.3	61.1

^a Note: g-mean denotes geometric mean.

representative of the majority of LUFT sites in California, statistical analyses of site hydrogeology and contaminant impact were conducted in manner similar to Happel et al. (1) and reported in detail in text and figures in the Supporting Information.

2.4. Analytical Methods. The analysis of oxygenates as a group using conventional analytical procedures designed for petroleum hydrocarbons has been shown to be problematic (1, 20). USEPA Method 8020/21B, a protocol routinely employed for the analysis of LUFT samples, was unfit for monitoring of TBA and frequently yielded false-positive and inaccurate results when ether oxygenates were monitored in aqueous samples containing high TPH_c concentrations ($>1000 \mu\text{g L}^{-1}$). In contrast, Halden et al. (20) demonstrated that USEPA Method 8260B (gas chromatography/mass spectrometry) was a robust protocol for oxygenates over a wide range of TPH_c background concentrations. To ensure that appropriate protocols for the analysis of oxygenates were utilized, only those groundwater samples from LUFT sites that had been analyzed for BTEX and ether and alcohol oxygenates using USEPA Method 8260B were used for this study. TPH_c was analyzed using USEPA Method 8015 nonaromatic, nonhalogenated chromatograph procedure. Laboratory MDLs for TPH_c, BTEX, TBA, and ether oxygenates were set at 100, 1, 10, and $2 \mu\text{g L}^{-1}$, respectively.

3. Results and Discussions

3.1. Occurrence and Distribution of FHCs and Oxygenates at LUFT Sites. To determine the frequency of detection of FHCs and oxygenates at LUFT sites, their maximum site

concentrations, and the correlation among these gasoline constituents, groundwater monitoring data from over 7200 monitoring wells in EDF were analyzed from 868 LUFT sites in the greater Los Angeles region. At a reporting limit of 100, 1, 10, and $2 \mu\text{g L}^{-1}$, for TPH_c, benzene, TBA, and ether oxygenates, respectively, 96% of the EDF-LUFT sites contained at least one FHC or oxygenate, 92% contained at least two analyzed compounds, 60% contained at least four compounds, and 1.5% contained all seven FHC and oxygenate compounds. TPH_c was the analyte most frequently detected at 91.8% of EDF-LUFT study sites, followed by MTBE and benzene at 82.7% and 82.5%, TBA at 61.1%, and the alternative ether oxygenates DIPE, TAME, and ETBE at 23.7%, 18.3%, and 8.9%, respectively.

The site maximum analyte concentration (SMAC) was a good indicator of the source analyte concentration or strength in groundwater. SMAC was determined for each of the seven FHCs and oxygenates at individual EDF-LUFT study sites. Figure 1 depicts a comparison of the SMAC cumulative distributions. The results indicate that, excluding the composite measure TPH_c, TBA has the greatest site maximum concentrations, followed by MTBE/benzene and DIPE, TAME, and ETBE. The mean, geometric mean, median, and other relevant measures are displayed in Table 1 for LUFT sites with detectable levels of analyte. The log-normality of the data sets, confirmed by graphical tools and more quantitative measures (e.g., coefficient of variation, the Shapiro-Wilk Test (21), and skewness), necessitated a natural log data transformation before computation of the *t*-test (21—

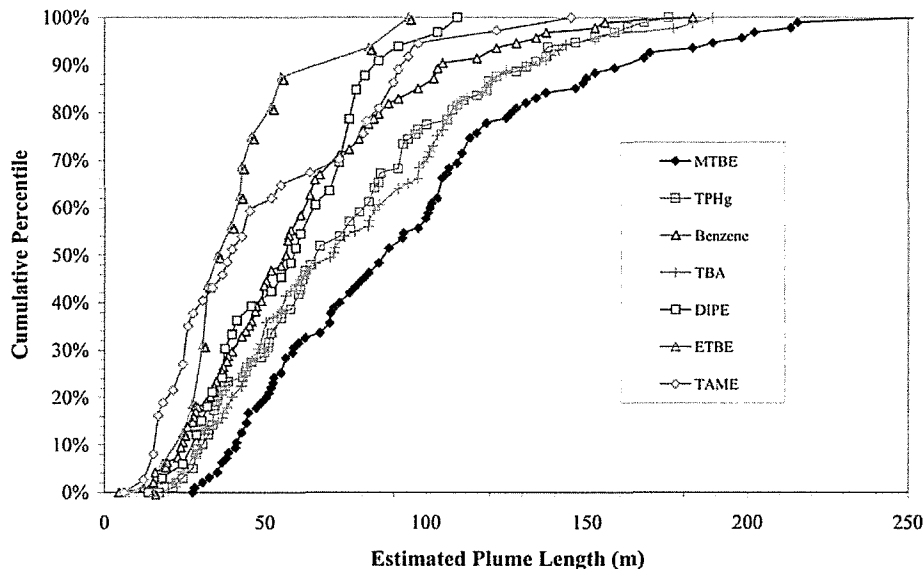


FIGURE 2. Plot of plume length cumulative percentile for FHCs (TPH_c and benzene) and oxygenates (MTBE, TBA, DIPE, ETBE, and TAME). Note: benzene, ether oxygenate, TBA, and TPH_c plume lengths were defined to 5, 5, 10, and 100 $\mu\text{g L}^{-1}$ dissolved concentration contours, respectively.

23) to examine the significance of variations in concentration observed among the FHC and oxygenate compounds. Bonferroni probability (*Bon. p*) was provided as protection for performing multiple *t*-tests simultaneously. Among the FHC and oxygenates, TPH_c has the greatest geometric mean site maximum concentration, followed by TBA, MTBE, benzene, and the ether oxygenates DIPE, TAME, and ETBE (Table 1), confirming what is observed in Figure 1. The student *t*-test verified statistically significant ($\alpha = 0.05$, *Bon. p* < 0.05) differences for 20 out of 21 possible pairwise comparisons among the seven FHC and oxygenate compounds.

The study observations indicate low concentrations of alternative ether oxygenates (DIPE, ETBE, and TAME) at LUFT sites (e.g., 50% of the detected maximum site concentrations for ETBE, TAME, and DIPE were less than 5, 20, and 30 $\mu\text{g L}^{-1}$, respectively (Figure 1)). Examinations of gasoline surveys provide definitive knowledge of which oxygenate and what volumes of that oxygenate are being used in a particular region of the country. As demonstrated by the 1995–1997 EPA Oxygenate Type Analysis and RFG Survey Data (24), the quantity of alternative ether oxygenates (DIPE, ETBE, and TAME) in Los Angeles area gasoline are near trace amounts (<1% by weight), which may explain their low soluble source concentrations observed.

In addition, high TBA source concentrations were observed. In fact, excluding the composite measure TPH_c, TBA has the greatest geometric mean site maximum groundwater concentration among our study analytes. This finding may be explained in terms of the solubility and sources of TBA. Even though TBA was added to gasoline in significantly lesser amounts than MTBE or benzene, its high miscibility meant that small quantities of TBA could translate into high groundwater concentrations. Further, different sources of TBA (as gasoline additive, impurity, or oxidation byproduct of MTBE) could by themselves, or in combination, result in the detected TBA in groundwater at LUFT sites.

3.2. Characterization of Contaminant Spatial Extent at LUFT Sites. Contaminant plume length was used as an initial indicator of the threat of contamination to drinking water sources by contaminants present in shallow groundwater at LUFT sites and was estimated according to procedures in section 2.1.1. Figure 2 presents FHC and oxygenate plume lengths in terms of cumulative percentile. The results indicate

that among the FHCs and oxygenates, MTBE has the greatest plume length, followed by TBA/TPH_c, benzene, and the alternative oxygenates DIPE, TAME, and ETBE. The difference in plume length is clearly distinguishable, as in the case of MTBE versus FHC and MTBE versus other oxygenates. In contrast, pairwise comparisons between TBA/TPH_c, benzene/DIPE, and TAME/ETBE cumulative distributions indicate that for these pairs, the variation in plume length is difficult to distinguish as demonstrated by the overlapping cumulative percentile curves.

The statistical significance of the plume length differences among the FHC and oxygenate groups was examined using the two sample *t*-test (after log-transformation). The log-normality of the data sets indicates that the geometric mean and the median are better descriptors of the LUFT plume population. Table 2 summarizes the data. Among the FHC and oxygenates, MTBE has the greatest geometric mean plume length at 83 m, followed by TPH_c/TBA at 64 and 63 m, benzene/DIPE at 51 and 50 m, and TAME/ETBE at 36 and 34 m. The student *t*-test verified statistically significant ($\alpha = 0.05$, *Bon. p* < 0.05) differences for pairwise comparisons of MTBE and TBA to DIPE, ETBE, and TAME as well as comparisons between MTBE and TBA, MTBE and benzene, and TBA and benzene. In contrast, pairwise comparisons of DIPE, ETBE, and TAME to one another as well as benzene to DIPE or ETBE were not.

Contaminant groundwater plume length is influenced by factors such as hydrogeologic characteristics, matrix chemical interactions, source strength, biodegradation, and intrinsic properties of the chemical of interest. Under steady-state conditions, the differences in plume length among the FHCs and oxygenates at a particular site may be attributed primarily to differences in source strength and degradability of the contaminant. The lower source strengths of alternative ether oxygenates (DIPE, ETBE, and TAME) (Figure 1) as compared to MTBE, TBA, or FHCs may have contributed in large part to the observed localization of these plumes. In contrast, since the FHCs have source strengths of similar magnitudes as compared to MTBE and TBA (Figure 1), it is likely the significantly greater biodegradability of the FHCs (TPH_c and benzene) relative to TBA and ether oxygenates favored the more restricted plume migrations from the source areas as compared to MTBE and TBA plumes.

TABLE 2. Summary Statistics on Estimated LUFT Site Analyte Plume Length in Groundwater^a

	MTBE (5 µg L ⁻¹)	TPH _C (100 µg L ⁻¹)	benzene (5 µg L ⁻¹)	DIPE (5 µg L ⁻¹)	ETBE (5 µg L ⁻¹)	TAME (5 µg L ⁻¹)	TBA (10 µg L ⁻¹)
facilities (n)	96	99	95	34	17	37	86
min (m)	26	11	7	14	15	6	15
max (m)	317	259	168	119	94	137	192
median (m)	84	66	51	58	35	40	61
mean (m)	96	75	60	55	39	47	73
<i>g</i> -mean (m)	83	64	51	50	34	36	63

^a Note: *g*-mean denotes geometric mean.

TABLE 3. Change in Analyte Groundwater Plume Length over Time (1 year)^a

	MTBE (5 µg L ⁻¹)	TPH _C (100 µg L ⁻¹)	benzene (5 µg L ⁻¹)	DIPE (5 µg L ⁻¹)	ETBE (5 µg L ⁻¹)	TAME (5 µg L ⁻¹)	TBA (10 µg L ⁻¹)
case (n)	96	99	94	33	16	35	86
<i>g</i> -mean change (m)	-1.5	-0.3	0.6	0	1.5	1.2	3.7
<i>g</i> -mean (m)	83	64	51	50	34	36	63
% change	-1.8	-0.5	1.2	0	4.4	3.3	5.9
<i>P</i> value	0.28	0.89	0.61	0.94	0.58	0.19	0.06

^a Note: negative *g*-mean change indicates that the plume length for the selected analyte decreased over time, while positive *g*-mean change indicates the opposite.

3.3. Time Series Analysis of Contaminant Spatial Extent at LUFT Sites. Contaminant plume lengths in groundwater were tracked for 1 year for a population of LUFT sites (section 2.1.2 for site selection). A total of 464 individual plumes were tracked resulting in a total of 1856 plume lengths estimated over four quarters (Figure S3, Supporting Information). Comparison of the cumulative percentile (CP) curves over four quarters indicate that for MTBE, TPH_C, and benzene, the overlapping CP curves suggest the changes in plume length over this time period are not discernible—either the plume lengths are stable or the time period examined is not sufficient for changes to develop and/or be detected. In contrast, comparison of the CP curves for the alternative oxygenates ETBE, TAME, and TBA indicates a somewhat discernible trend of increasing plume lengths over the 1-year period. This trend is most apparent in the case of TBA, where the plume length increase over 1 year is ~6%. Decreases in contaminant plume length beneath LUFT study sites over time are likely to be the result of decreasing source strength from ongoing source removal and cleanup as well as biodegradation. Increases in contaminant plume length over time, on the other hand, may be due to a variety of factors. The more recent release of gasoline formulations containing significantly greater quantities of oxygenates may not have afforded sufficient time for oxygenate plumes to reach maximum plume configurations. As for TBA, since it is also a degradation product of MTBE, it is possible that as the MTBE plume farther away from the source area continues to degrade into TBA at concentrations above detection limit; these changes in TBA concentration would be detected by the peripheral monitoring network and thus result in increases in plume length contour.

To assess whether the plume length differences that develop over time were statistically significant, paired *t*-tests were performed (after log-transformation) for each FHC and oxygenate compound. The results indicate that after 1 year, none of the plume length differences that occurred during this period was significant at $\alpha = 0.05$ (Table 3).

Rice et al. (25) conducted a trend analysis for benzene plume lengths with time and determined that approximately 60% of the sites studied contained no significant temporal trends, while 32% and 8% of the sites have decreasing and increasing temporal trends, respectively. While the vast majority of benzene and TPH_C plumes are apparently stable

(1, 25), it remains to be seen whether oxygenate plumes have reached steady state. The different release histories of these compounds can be a factor in interpreting the plume length results. If the oxygenate plumes have not reached steady state, then the observed plume length results may not be indicative of future plume lengths. Time-series analysis of plume length data presented in this paper does lend some support to the stability of the plumes, FHC or oxygenate. However, substantially longer time-series analyses are needed to verify this assumption.

3.4. Impact of Fuel Oxygenates on FHC Plume Lengths. Several laboratory, modeling, and small-scale case studies have been conducted to investigate the impact of ethanol on FHC plumes (26–28). It has been demonstrated that high concentrations of ethanol have the potential to increase the spatial extent of FHC plumes primarily through (1) the reduction in the biotransformation rates of FHC attributed to a reduction of available electron-acceptor species that participate in biogeochemical oxidation/reduction reactions (27) and (2) increases in the solubility of FHCs through a cosolvency effect (26). To investigate whether the presence of fuel oxygenates other than ethanol can influence the mobility and spatial extents of FHC in a similar manner, two distinct populations of LUFT sites were identified. One population was composed of LUFT sites where oxygenates had been used or detected, versus another where none of the five oxygenates of interest had been used or detected (see section 2.1.2 for site selection/protocol). Figure 3 compares the FHC plume lengths at “FHCs only” versus at “FHCs and oxygenates” LUFT sites. A student *t*-test (after log-transformation) was used to test the significance of variations in TPH_C and benzene plume lengths between the two populations of LUFT sites. The results indicate that TPH_C and benzene plumes are significantly (at $\alpha = 0.1$) longer (+20–30%) in the presence of oxygenates.

By comparing FHC (TPH_C and benzene) plume lengths at LUFT sites that differ only in one respect (e.g., the presence or absence of oxygenates), an attempt was made to adjust for other differences between the population of LUFT sites. However, the presence or absence of oxygenates at LUFT sites may itself be indicative of the relative age of the spill. Not until the passage of 1990s CAA mandating the use of RFG or oxyfuel has the addition of oxygenate been so widespread and at such a dramatic scale. Consequently, LUFT

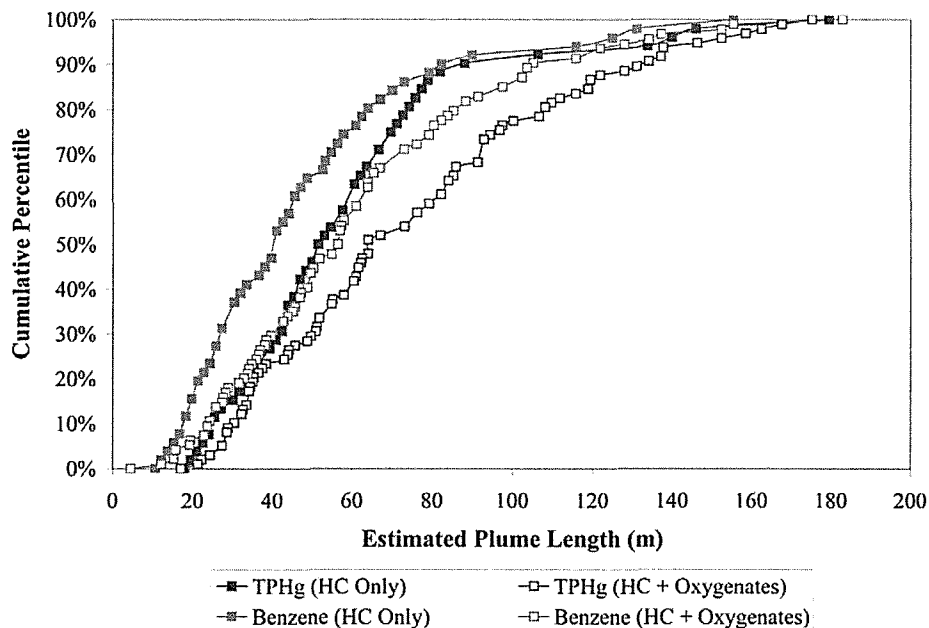


FIGURE 3. Comparison of TPH_G and benzene plume lengths at "hydrocarbons only" versus at "hydrocarbons and oxygenates" LUFT sites. TPH_G and benzene plume lengths were defined to 100 and 5 $\mu\text{g L}^{-1}$ dissolved concentration contours, respectively.

sites contaminated with both FHCs and oxygenates tend to have at least one or more recent fuel release(s). Conversely, LUFT sites impacted by only FHCs tend to have more aged source zones created by older spills from gasoline without oxygenate additives. Differences in the age of the spill can influence the length of FHC plumes since LUFT sites with more aged source zones also tend to have plumes that, relative to plumes at newer source zones, are stabilized or shrinking. Future work is needed to determine whether the increase in the FHC spatial extent is caused by the presence of oxygenates (e.g., through the mechanism of competition for electron acceptor species or the cosolvency effect) or is merely an artifact created by the inherent differences in the age of the spill resulting from the study design of separating LUFT sites into discrete populations ('FHCs-only' versus 'FHCs and oxygenates').

4. Implications

The site detection frequencies and maximum groundwater concentrations for TBA, MTBE, and benzene were elevated. While the groundwater samples beneath LUFT sites across the states frequently are analyzed for a suite of FHC (e.g., BTEX) and some oxygenate (e.g., MTBE) compounds, the analysis for other oxygenates in most states has seldom been performed. Site groundwater concentrations and plume length data indicate TBA contamination at a scale similar to MTBE. In addition, due to its physical/chemical properties, TBA is often the regulatory driver for treatment considerations at LUFT sites. Therefore, the presence of TBA needs to be confirmed at gasoline-impacted sites, and if confirmed, a specific cleanup strategy needs to be developed that accounts for its presence along with any other FHC or oxygenate compounds that are present. In contrast to benzene, MTBE, and TBA, the site detection frequencies and maximum groundwater concentrations for alternative ether oxygenate DIPE, ETBE, and TAME beneath LUFT facilities were low. Plume length comparisons also indicate these alternative ether oxygenates to be localized relative to MTBE, TBA, or FHCs. Even though data from this study suggests that current risk from the alternative ether oxygenates to groundwater resources at LUFT sites should be minimal, caution should be applied against over-interpretation of the data in anti-

cipating the consequences of possible scale-up in usage of these compounds. An appropriate parallel may be found in the progression of the MTBE problem. Prior to the 1990s, when MTBE was used primarily as an octane booster, it made up only 1–3% by volume of some gasoline. It was only after the scale of MTBE usage escalated in response to the 1990s CAA Amendments that the environmental consequences associated with its use became apparent. All indications (e.g., physical/chemical characteristics such as high solubilities and low biodegradabilities (relative to FHCs)) suggest that the alternative ethers would pose groundwater contamination threats similar to MTBE if their scales of usage were expanded.

With the staggering number of LUFT facilities located in close proximity to community drinking water sources, LUFT sites represent major point sources of gasoline constituents and the leading cause of FHC and oxygenate groundwater contamination. There is little doubt that a large proportion of underground storage tank (UST) systems at gasoline stations leak, and that is apparently true even for upgraded, double-tank systems. The number of leaks indicates that the problem is primarily in the design of the system, which arises from real estate limitations, fire defense considerations, and a defense against accidents and vandalism (29). In the absence of completely new design and construction of the system that emphasizes detection, repair, and containment, an effective management strategy may involve placing greater emphasis on a UST program for ensuring adequate enforcement and compliance with existing UST regulations. In California, existing UST regulations require, specifically, the upgrading of USTs and the institution of leak detection systems. The plume lengths data indicate that under a well-managed UST program, with prompt detection and cleanup of source contaminants associated with failed UST systems, FHC and oxygenate plume lengths in the hundreds of meters were quite rare. The overwhelming majority of plumes associated with release(s) from LUFT facilities were relatively "localized". For instance, an examination of plume lengths of alternative ether oxygenate DIPE, ETBE, and TAME found 90% of the plumes were less than 100 m from the source area. Even in the case of MTBE, 90% of the MTBE plumes were observed to be less than 165 m. The adequate compliance with existing UST regulations may decrease the prob-

ability of future leakage and allow for prompt response and cleanup of possible sources. This scenario could provide adequate safeguard against widespread and catastrophic impact of FHC and oxygenate plumes on groundwater sources since under these conditions the FHC and oxygenate plumes are likely to be localized.

Acknowledgments

Assistance for this project was provided by David Bacharowski, Joe Luera, Nhan Bao, and Sapna Hiranandani of CRWQCB-LA. The authors would also like to acknowledge the work previously conducted by Ann Happel, Brenden Dooher, and Dave Rice of Lawrence Livermore National Laboratory. This work followed some of their methods in delineating the environmental impacts from LUFT populations (1, 26).

Supporting Information Available

Analyses of site setting and representativeness and correlation among SMAC and among contaminant plume lengths are reported in detail in text, tables, and figures in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Happel, A. M.; Beckenbach, E. H.; Halden, R. U. *An Evaluation of MTBE Impacts to California Groundwater Resources*; 1998; UCRL-AR-130897.
- (2) Squillace, P. J.; Zogorski, J. S.; Wilber, W. G.; Price, C. V. *Environ. Sci. Technol.* **1996**, *30*, 1721–1730.
- (3) *The Report of the Blue Ribbon Panel on Oxygenates in Gasoline*; 1999; EPA 420-R-99-021.
- (4) Franklin, P. M.; Koshland, C. P.; Lucas, D.; Sawyer, R. F. *Environ. Sci. Technol.* **2000**, *34*(18), 3857–3863.
- (5) Johnson, R.; Pankow, J.; Bender, D.; Price, C.; Zogorski, J. *Environ. Sci. Technol.* **2002**, *34*(9), 210A.
- (6) Rong, Y. *Environ. Forensics* **2001**, *2*, 9–11.
- (7) Deeb, R. A.; Hu, H. Y.; Hanson, J. R.; Scow, K. M.; Cohen, L. A. *Environ. Sci. Technol.* **2001**, *35*, 312–317.
- (8) Mormile, M. R.; Liu, S.; Sulflita, J. M. *Environ. Sci. Technol.* **1994**, *28*, 1727–1732.
- (9) Yeh, C. K.; Novak, J. T. *Water Environ. Res.* **1994**, *66*, 744–756.
- (10) Squillace, P. J.; Pankow, J. F.; Korte, N. E.; Zogorski, J. S. *Environ. Toxicol. Chem.* **1997**, *16*, 1836–1844.
- (11) Fayolle, F.; Vandecasteele, J. P.; Monot, F. *Appl. Microbiol. Biotechnol.* **2001**, *56*, 339–349.
- (12) Squillace, P. J.; Moran, M. J.; Lapham, W. W.; Price, C. V.; Clawges, R. M.; Zogorski, J. S. *Environ. Sci. Technol.* **1999**, *33*(23), 4176–4187.
- (13) Stocking, A.; Suffet, I. H.; McGuire, M. J.; Kavanaugh, M. *AWWA* **2001**, *93*(3), 95–105.
- (14) Deeb, R. A.; McMillan, B.; Kavanaugh, M. C. *Environmental Fate and Transport of Fuel Oxygenates*; Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Groundwater, 2001, Houston, Texas.
- (15) Ellis, P. *A Circle Vicious: what do we know about the other oxygenates?* New England Interstate Water Pollution Control Commission, L.U.S.T.LINE, Bulletin 37, March 2001.
- (16) Happel, A.; Dooher, B.; Beckenbach, E. *MTBE Impacts to California Groundwater*; USEPA Blue Ribbon Panel, March 25, 1999. UCRL-MI-133696.
- (17) Williams, P. R. D.; Sheehan, P. J. *AEHS Contaminated Soil Sediment & Water*; spring 2001, pp 23–28.
- (18) Dooher, B. P. *Screening Analysis of Potential Groundwater Resource Impacts from Gasoline Containing Ethanol or MTBE*; 1999, UCRL-AR-135949.
- (19) California Regional Water Quality Control Board—Los Angeles. *General Laboratory Testing Requirements for Petroleum Hydrocarbon Impacted sites*; June 5, 2000.
- (20) Halden, R. U.; Happel, A. M.; Schoen, S. R. *Environ. Sci. Technol.* **2001**, *35*(7), 1469–1474.
- (21) Bohrnstedt, G. W.; Knoke, D. *Statistics for Social Data Analysis*; F. E. Peacock Publishers, Inc.: Itasca, IL, 1988.
- (22) Rong, Y. *Environ. Geosci.* **1997**, *4*(3), 149–152.
- (23) Rong, Y. *Environ. Forensics* **2000**, *1*, 213–220.
- (24) USEPA 1995 and 1996 Oxygenate Type Analysis RFG Survey Data. <http://www.epa.gov/otaq/consumer/fuels/mtbe/oxy-95-00.pdf>
- (25) Rice, D. W.; Grose, R. D.; Michaelson, J. C.; Dooher, B. P.; MacQueen, D. H.; Cullen, S. J.; Kastenburg, W. E.; Everett, L. E.; Marino, M. A. *California Leaking Underground Fuel Tank Historical Case Analyses*; 1995; UCRL-AR-122207.
- (26) Rice, D.; Powers, S. E.; Alvarez, P. J. *Potential Scenarios for Ethanol-containing Gasoline released into Surface and Sub-surface Waters*; 1999; UCRL-AR-135949.
- (27) Alvarez, P. J.; Hunt, C. S. *The effect of ethanol on BTEX biodegradation and natural attenuation*; 1999; UCRL-AR-135949.
- (28) McNab, W.; Heermann, S. E.; Dooher, B. *Screening Model Evaluation of the Effects of Ethanol on Benzene Plume Lengths*; 1999; UCRL-AR-135949.
- (29) Green, J. *Soil, Sediment & Groundwater*; MTBE special issue, March 2000.

Received for review May 9, 2003. Revised manuscript received September 5, 2003. Accepted October 1, 2003.

ES0304650