

# A Comparison of Benzene and Toluene Plume Lengths for Sites Contaminated with Regular vs. Ethanol-Amended Gasoline

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## Abstract

This article describes various statistical analyses of plume-length data to evaluate the hypothesis that the presence of ethanol in gasoline may hinder the natural attenuation of hydrocarbon releases. Plume dimensions were determined for gasoline-contaminated sites to evaluate the effect of ethanol on benzene and toluene plume lengths. Data from 217 sites in Iowa (without ethanol; set 1) were compared to data from 29 sites in Kansas that were contaminated by ethanol-amended gasoline (10% ethanol by volume; set 2). The data were log-normally distributed, with mean benzene plume lengths ( $\pm$  standard deviation) of  $193 \pm 135$  feet for set 1 and  $263 \pm 103$  feet for set 2 (36% longer). The median lengths were 156 feet and 263 feet (69% longer), respectively. Mean toluene plume lengths were  $185 \pm 131$  feet for set 1 and  $211 \pm 99$  feet for set 2 (14% longer), and the median lengths were 158 feet and 219 feet (39% longer), respectively. Thus, ethanol-containing BTEX plumes were significantly longer for benzene ( $p < 0.05$ ), but not for toluene. A Wilcoxon signed rank test showed that toluene plumes were generally shorter than benzene plumes, which suggests that toluene was attenuated to a greater extent than benzene. This trend was more pronounced for set 2 (with ethanol), which may reflect that benzene attenuation is more sensitive to the depletion of electron acceptors caused by ethanol degradation. These results support the hypothesis that the presence of ethanol in gasoline can lead to longer benzene plumes. The importance of this effect, however, is probably site-specific, largely depending on the release scenario and the available electron acceptor pool.

## Introduction

The use of ethanol as a gasoline additive is likely to increase in the near future as a substitute for the oxygenate MtBE (Powers et al. 2001a, 2001b). Regulatory renewable fuel requirements will also lead to additional ethanol use. Therefore, it is important to understand how ethanol affects the fate and transport of hydrocarbons in ground water. Previous laboratory studies have shown that the presence of ethanol could have undesirable effects on the biodegradation of BTEX (i.e., benzene, toluene, ethylbenzene, and *ortho*-, *para*-, and *meta*-xylene). Specifically, ethanol is often degraded preferentially and contributes to the depletion of nutrients and electron acceptors (e.g.,  $O_2$ ) that would otherwise be available to support BTEX biodegradation (Corseuil et al. 1998; da Silva and Alvarez 2002; Ruiz-Aguilar et al. 2002). In addition, high ethanol concentrations (>10%), which could occur initially at the source, could also enhance BTEX solubility and decrease sorption-related retardation, enhancing hydrocarbon migration (da Silva and Alvarez 2002; Powers et al. 2001b; Rao et al. 1990). These findings suggest that ethanol may hinder BTEX natural attenuation, which could result in longer BTEX plumes

and a greater risk of exposure. Nevertheless, little is known about the magnitude and significance of this potential plume-elongation effect.

Plume dimensions and stability are important parameters to characterize for risk management because they determine the area of influence and the potential duration of exposure. Several investigators have developed mathematical models for predicting the effect of ethanol (added to gasoline at 10% by volume) on BTEX plume length (Table 1). These screening models predict that ethanol would increase the maximum BTEX plume length (i.e., when steady state is reached) by anywhere from ~10% to 150%. Whereas these models provide valuable insight into the potential ground water impacts of ethanol in gasoline, they are based on simplifying and influential assumptions and have not yet been validated with field data. Therefore, there is a need for empirical evaluations of the effect of ethanol on BTEX plume length.

This article describes statistical analyses of plume-length data to evaluate the general hypothesis that the presence of ethanol in gasoline hinders the natural attenuation of hydrocarbons, resulting in longer BTEX plumes compared to reg-

**Table 1**  
Modeling Efforts to Assess the Effect of Ethanol on Benzene Plume Length

Citation	Conceptual Model	Increase in Benzene Plume Length
Heermann and Powers (1996)	2-D transport from a pool of gasoline. Focus on cosolvency and interface mass transfer. Biodegradation not included.	≤ + 10% (for xylene not benzene)
Malcom Pirnie Inc. (1998)	Steady-State, 2-D transport from a gasoline pool. First-order decay of benzene when $C_{EtOH} < 3 \text{ mg l}^{-1}$ . First-order decay of ethanol.	+ 17-34 %
McNab et al. (1999)	3-D aqueous transport. Continuous slow release of gasoline (up to 3 gpd) to a growing NAPL pool at the water table. First-order decay of ethanol and benzene. Benzene degradation rate constant defined by inverse correlation to BOD conc. at the source.	~ + 100 %
Molson et al. (2002)	3-D transport from a gasoline source at the water table at a residual saturation. Aerobic decay with $O_2$ as the sole electron acceptor quantified by Monod kinetics. Microbial growth incorporated.	+ 10–150 %

ular-gasoline releases. This article also addresses the likelihood that ethanol would hinder the natural attenuation of benzene to a greater extent than toluene due to differences in their biodegradability under the strictly anaerobic conditions induced by ethanol.

## Methodology

### Plume Data

Two sets of ground water data were collected from about 600 gasoline-contaminated sites. One of the data sets (set 1) was obtained from the Iowa Department of Natural Resources, Underground Storage Tanks Section (IDNR TIER-2 database). This database contained no information about the presence of ethanol; thus, the data were screened to exclude sites with suspected contamination by ethanol-amended gasoline. A review of site investigation reports and telephone surveys were conducted for this purpose. Many of the set 1 sites were also discarded because of insufficient data to plot the required plume contours (e.g., plumes not bracketed by downgradient wells) or because contamination resulted from multiple sources (e.g., overlapping plumes). Therefore, only 217 Iowa sites (contaminated with regular gasoline) were included in set 1. The other data set (set 2) was obtained from the Kansas Department of the Environment and Health (KDEH), and corresponded to 29 sites contaminated with gasohol (i.e., gasoline with 10% ethanol by volume). Site investigation reports did not show salient differences between the two data sets regarding release and response scenario (e.g., amount released, age of spill, or remedial activities). None of these sites reported MTBE contamination. In addition, MTBE is unlikely to affect BTEX or ethanol degradation in contaminated aquifers

(da Silva and Alvarez 2002; Deeb et al. 2001; Ruiz-Aguilar et al. 2002). Thus, MTBE was not a factor in this study.

### Determination of Plume Lengths

Benzene and toluene plume lengths were determined by contouring data from monitoring wells (which were typically separated by about 100 feet), using a computer algorithm based on Hardy's multiquadric method for plotting two-dimensional concentration contours (Saunderson 1994). This algorithm was incorporated into the Iowa RBCA TIER2 Interpolation Program version 2.17, which interfaces with the IDNR TIER-2 database. This approach eliminated subjectivity associated with drawing the plumes by hand. Selected computer-generated plumes were compared to the corresponding hand-drawn plumes for validation purposes. Plume lengths were then measured as the longest distance between the identified source and the 5 µg/L contour, which corresponds to the drinking water standard for benzene.

### Statistical Analyses

Plume length data were imported into Minitab (version 13.1, State College, Pennsylvania), which was used to calculate population statistics for each data set. These statistics included the population mean, standard deviation, median, maximum, and minimum. Distribution analyses were performed using the Anderson-Darling test for log-normality at the 95% significance level (Freedman et al. 1998). A Kruskal-Wallis test was also performed to determine whether BTEX plumes were significantly longer in set 2 (with ethanol) than in set 1 (without ethanol). This nonparametric test, which ranks plume lengths from low to high and then analyzes the ranks (Lehmann 1975), is very robust to test differences in population medians (Johnson and Mizoguchi 1978). Two-sample

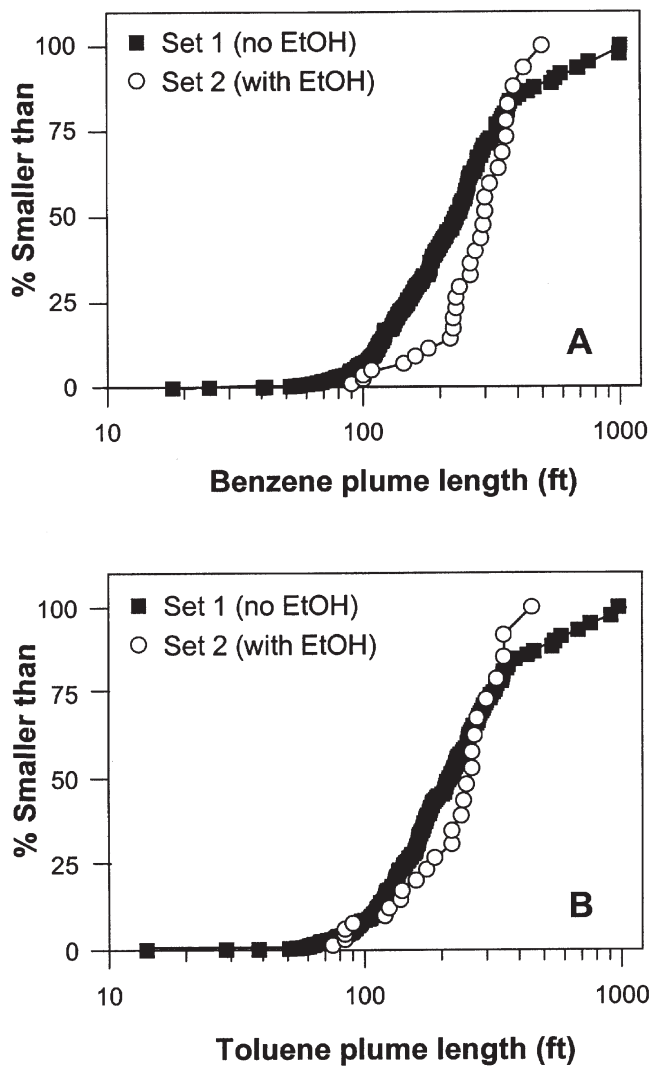


Figure 1. Cumulative distribution of (a) benzene and (b) toluene plume lengths for set 1 (Iowa data, without ethanol) and set 2 (Kansas data, with ethanol).

Student's t-tests (Freedman et al. 1998) were also performed to determine if average benzene and toluene plume lengths were significantly different between the two data sets. Finally, a Wilcoxon signed-rank test was performed to test if benzene plumes were generally longer than toluene plumes, and to determine if this trend was statistically significant.

## Results and Discussion

Plume length data were log-normally distributed ( $p = 0.275$  for benzene and  $0.394$  for toluene) according to an Anderson-Darling test. The cumulative distribution of the plume lengths shows that benzene plumes were generally longer for set 2 (with ethanol) than for set 1 (without ethanol) (Figure 1a). For example, 92% of benzene plumes in set 2 were longer than 150 feet, compared to only 74% for set 1. The same trend was observed for plumes longer than 250 feet. In this case, 69% of benzene plumes in set 2 were longer than 250 feet, compared to 45% for set 1. However, none of the 29 plumes in set 2 was longer than 500 feet, compared to 12% of the 217

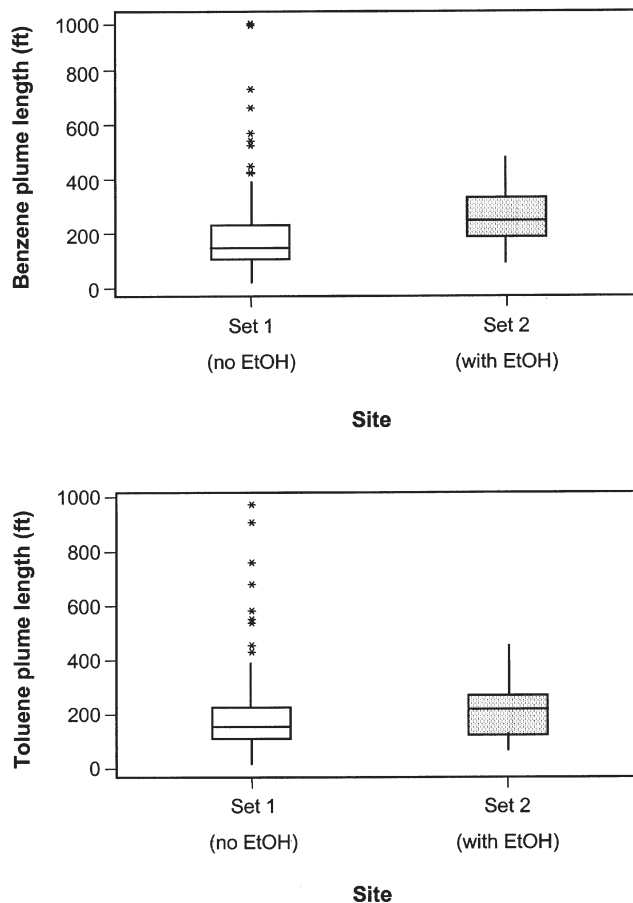


Figure 2. Box plots of the benzene and toluene plume length data. The line across the box represents the median. The bottom and top of the box represent the first and third quartiles (Q1 and Q3). The whiskers extend to the lowest and highest observations inside the region defined by  $Q1 - 1.5(Q3 - Q1)$  and  $Q3 + 1.5(Q3 - Q1)$ . Individual points with values outside these limits (outliers) are plotted with asterisks.

plumes in set 1. This trend reversal reflects that set 1 was a much larger data set and contained both the smallest and largest plumes. Note that these longer plumes are statistical outliers, as determined by the Tukey method (Tukey 1977; Figure 2). Similar results were observed for toluene, although the apparent elongation effect of ethanol was not as pronounced (Figure 1b).

Box plots corroborated that BTEX plumes with ethanol (set 2) were generally longer than those from set 1, without ethanol (Figure 2). A Kruskal-Wallis test showed that the median length of benzene plumes was significantly longer for set 2 than for set 1 (263 versus 156 ft  $p < 0.001$ ; Figure 3). On the other hand, the difference for toluene plumes was not statistically significant (219 versus 158 feet,  $p = 0.073$ ). Note that the median length for benzene and toluene plumes without ethanol is within 15% of that reported by Newell and Connor (1998) (i.e., 132 feet). This value was obtained from a compilation of four surveys (Groundwater Services 1997; Mace et al. 1997; Rice et al. 1995; Newell and Connor 1990), covering a total of 604 sites presumably contaminated with gasoline without ethanol.

Parameters	Compound			
	Benzene		Toluene	
	Set 1 (no EtOH)	Set 2 (with EtOH)	Set 1 (no EtOH)	Set 2 (with EtOH)
Number of sites	217	29	211	26
Minimum (ft)	18	90	14	75
Median (ft)	156	263	158	219
Maximum (ft)	1005	500	973	450
Mean (ft) ± Std. deviation	193 ± 135	263 ± 103	185 ± 131	211 ± 99
p – value	0.002*		0.243	

\*Data were significantly different ( $p < 0.05$ ) as determined by a two-sample student's t-test.

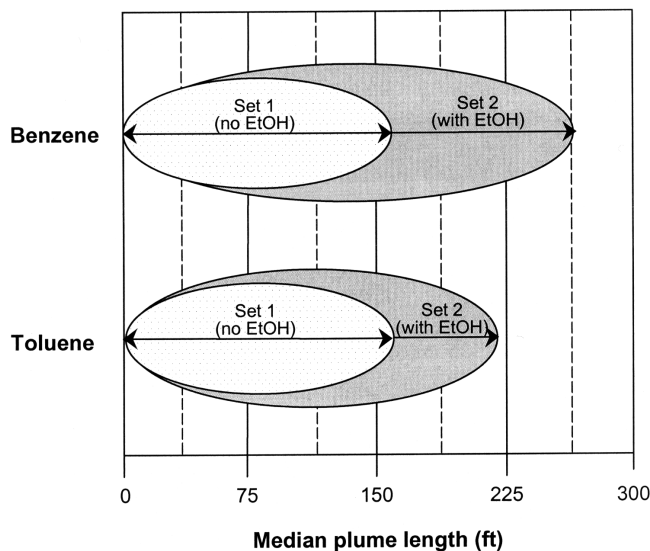


Figure 3. Median length of set 1 (Iowa data, without ethanol) versus set 2 plumes (Kansas data, with ethanol). The difference was significantly different for benzene ( $p < 0.001$ ), but not for toluene ( $p = 0.073$ ), as established by a Kruskal-Wallis test.

Table 2 summarizes the central tendencies of benzene and toluene plume lengths. The average length of BTEX plumes with ethanol was higher than the corresponding value without ethanol (by 36% or 70 feet for benzene, and by 17% or 26 feet for toluene). Similar to the Kruskal-Wallis test, two-sample student's t-tests showed that these differences were statistically significant for benzene ( $p = 0.002$ ) but not for toluene ( $p = 0.243$ ). Whereas an increase of 70 feet in the average length of benzene plumes is statistically significant, this does not imply that the corresponding increase in public health risk will also be significant.

Benzene plumes were generally longer than toluene plumes, and this difference was more pronounced for the data set with ethanol (set 2). Specifically, the average benzene plume was 20% longer than the average toluene plume for set 2, compared to a 4% difference for the data set without ethanol (set 1). A Wilcoxon signed rank test showed that both of these

Material	Percent of Sites Where Material was Dominant	
	Set 1 (no ethanol)	Set 2 (with ethanol)
	Clay	40
Limestone	4	0
Mixed	28	34
Sand	15	23
Shale	0	3
No data available	13	9

Dominant Aquifer Material	Number of sites	Benzene Plume Length	
		Average (ft)	Standard Deviation (ft)
<b>Set 1 (no ethanol, Iowa)</b>			
Clay	85	184	107
Limestone	8	155	105
Mixed	59	172	84
Sand	35	249	215
No data available	31	199	164
<b>Set 2 (with ethanol, Kansas)</b>			
Clay	8	242	89
Mixed	9	283	105
Sand	8	250	92
Shale	1	288	0
No data available	3	292	201

\*For a given set, differences between categories were not significantly different.

differences were statistically significant ( $p < 0.05$ ), which suggests that the potential elongating effect of ethanol could be more pronounced for benzene than for toluene (Figure 3). Benzene, which is the most toxic of the BTEX compounds, is relatively recalcitrant under the anaerobic conditions exacerbated by an ethanol-driven consumption of electron acceptors (Corseuil et al. 1998; Heider et al. 1998). Toluene is more frequently reported to degrade under anaerobic conditions. The methyl group in toluene is electrophilic and facilitates nucleophilic attack by water (Alvarez and Vogel 1995) or by anaerobic catabolic enzymes such as benzyl succinate synthase (Heider et al. 1998). This facilitates the initiation of degradation without the action of an oxygen requiring oxygenase enzyme. The higher biodegradability of toluene and its higher tendency than benzene to be retarded by sorption (Alvarez et al. 1998) are conducive to shorter plumes.

As is commonly the case for many epidemiological studies, it should be pointed out that the inferences of our statistical analysis are constrained by other factors besides the presence of ethanol that could influence plume length. Although Iowa and Kansas have a similar geologic history, unaccounted confounding factors include hydrogeologic and geochemical characteristics that control the rates of advection,



dilution, sorption, volatilization, and biodegradation, as well as site heterogeneity and the release and response scenarios. Unfortunately, logistical and cost constraints often preclude the quantification of these processes at gasoline-contaminated sites. Therefore, these factors could not be included in our statistical analysis, with the exception of considering borehole data that permitted the categorization of the sites according to the dominant type of aquifer material (Table 3). These data suggest that a slightly higher percentage of sites in set 1 were less permeable than in set 2 (i.e., 46% vs. 33% were clay-rich and 19% vs. 24% were sandy). Although plumes were generally longer in sandy than in clay-rich aquifers, the standard deviations for a given lithologic category were relatively large, as illustrated for benzene plumes (Table 4). Therefore, the dominant type of aquifer material did not have a statistically significant effect on plume length. This finding is consistent with previous plume studies (Rice et al. 1995; Mace et al. 1997). This does not mean that the type of aquifer material (and its associated permeability and sorption capacity) does not affect plume length. Rather, it implies that other factors that were not quantified could be more influential.

In spite of the many potentially confounding factors associated with field data, it should be recognized that (1) such confounding factors were likely randomized by the relatively large data set considered; (2) Kansas plumes were longer even though temperatures tend to be slightly warmer in Kansas than in Iowa, which is conducive to faster biodegradation; and (3) the results of the statistical analysis show a strong consistency of association with experimental and modeling results and with biologically plausible explanations discussed previously. Therefore, this work supports the hypothesis that the presence of ethanol in gasoline can lead to longer benzene plumes. These results should provide a basis for further field studies involving controlled gasohol releases to improve our gasohol-release risk assessment capabilities.

## Conclusion

This study investigated the potential magnitude and significance of BTEX plume elongation by the presence of ethanol in gasoline. There was a statistically significant difference in mean benzene plume lengths between gasoline- versus gasohol-contaminated sites. The mean toluene plume lengths were not significantly different. Ethanol apparently hinders the biodegradation of benzene to a greater extent than toluene because benzene is less degradable under strictly anaerobic conditions that are exacerbated by the depletion of electron acceptors during ethanol degradation. The significance of this effect, however, is probably site-specific, largely depending on the release scenario and the available electron acceptor pool.

## Acknowledgments

We thank Greg Hattan (KDHE) for providing the Kansas data, Jim Humeston (IDNR) for the Iowa data. Rich Keller, Jose Fernandez, Jason Assouline, Russ Sawvel, and Zeb Squires are gratefully acknowledged for their help in data processing, and Steve Hillis for valuable advice about the statistical analysis. This project was funded by the American

Petroleum Institute and by the U.S. Environmental Protection Agency.

## Biographical Sketches

**Graciela Ruiz-Aguilar** is a post-doctoral fellow in the Department of Civil and Environmental Engineering at the University of Iowa, where she is conducting research on the anaerobic bioremediation of BTEX-ethanol mixtures. She has a Ph.D. in biotechnology and bioengineering from the Instituto Politecnico Nacional-CINVESTAV, in Mexico City, Mexico. Her studies focused on fungal technologies for PCB degradation

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