Implications of MTBE for Intrinsic Remediation of Underground Fuel Tank Sites

Joseph E. Odencrantz

Joseph E. Odencrantz, Ph.D., P.E., is a registered civil engineer with approximately 17 years of experience in the fields of environmental engineering and water resources. He is the founder and president of Tri-S Environmental, Sensible Strategies and Solutions for the Environment, Newport Beach, California. Address: 2121 Yacht Yankee, Newport Beach, California 92660.

MTBE in groundwater has been shown to travel over 1,000 feet downgradient from its source in several comprehensive field studies conducted across North America. The biodegradability of MTBE is examined by summarizing all the significant literature on the subject and by detailing the findings of recent field investigations of MTBE transport. In Orange County, California, the persistence of MTBE is analyzed and statistical representations of source variability are presented. Regional and far field transport of MTBE in groundwater sourced from underground gasoline storage tanks are summarized in comprehensive tables of frequency and plume length. Estimates of source mass and duration allow for comparison of associated plume size. The conclusion reached after reviewing all the available literature on MTBE is that its biodegradability seems slight and the size of the plumes are surprisingly large. Intrinsic or natural attenuation remedies for MTBE merit close scrutiny.

The issue of MTBE persistence in groundwater has been one of the most important topics of discussion in the remediation industry during the past year. MTBE biodegradability in groundwater is unclear and misunderstood due to the lack of applied research on the fundamental mechanisms of biodegradation. There are reports of an MTBE plume of over three miles in length (MacDonald, 1998) and due to its reported lack of any significant biodegradability, a significant regulatory problem indeed. The municipalities charged with public water supply sourced by groundwater are very concerned and the proposed action level for MTBE in groundwater is 35 µg/L (a possible carcinogen). Reported concentrations from groundwater monitoring wells of MTBE range from 10,000 to 50,000 µg/L on the high end (pure phase solubility approximately 51 million µg/L) are not uncommon. The petroleum industry is exploring alternatives and funding additional research.

REGIONAL MTBE GROUNDWATER OBSERVATIONS

As a general indication of the "scope" of the MTBE problem in groundwater, the results of a compilation of data from National Water Quality Assessment (NAWQA) are presented (data obtained from Squillace

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et al., 1995). **Exhibit 1** illustrates the predominance of MTBE in urban and agricultural regions throughout the United States during 1993-1995. There appears to have been early warning of a forthcoming problem with MTBE by examining its occurrence versus benzene (4.5 times more frequent). The 22 percent overall frequency of MTBE in urban wells and the 79 percent frequency in Denver is quite surprising for the time frame of the studies. Although the frequency of the shallow aquifers and agricultural wells are eight to twenty times, respectively, lower in frequency than the urban wells, the presence of MTBE tells all.

NEAR FIELD MTBE GROUNDWATER OBSERVATIONS

Mr. Ken Williams of the Santa Ana Regional Water Quality Control Board in Riverside, California was kind enough to share his compilation of MTBE data from groundwater monitoring wells at gasoline service station sites in Orange County, California in 1997. **Exhibit 2** illustrates the variation in maximum MTBE concentration at these sites by presenting the quarterly percent exceedences for various concentration values. Insight into the behavior of MTBE close to the source can be gleaned by examining the data used to generate Exhibit 2 in further detail. **Exhibit 3** shows the average of the quarterly values for each concentration threshold, which approximates the average maximum MTBE concentration for 1997. The linear line of best fit and the R squared value (97.15 percent) are also plotted on the graph. It is quite clear that the distribution is logarithmic and the percent exceedence distribution can be approximated by ln(MTBE in µg/L)*-0.0865+1.0805 and a final multiplication of 100 for percent conversion. The percent exceedence for 35 µg/L is 77.3 percent (i.e. 77.3 percent of the sites had a maximum MTBE concentration of at least 35 µg/L and 48.3 percent is the exceedence percentage for 1,000 µg/L).

Exhibit 4 is a plot of the 1997 coefficient of variation for each of the threshold concentrations for the maximum MTBE concentration at each

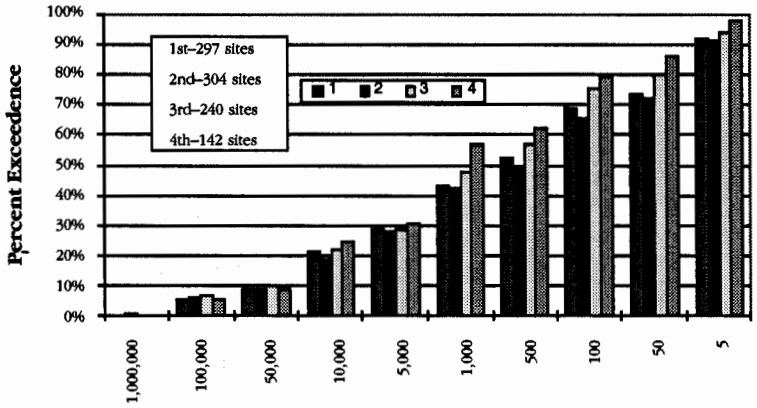
Exhibit 1. NAWQA's MTBE Results for Groundwater for 1993-1995

		CONCENTRATION PERCENTILES (µg/L)					
Samples	*Frequency*	*10th*	*50th*	*90th*	*95th*	*Max*	*Source*
304	22.0	< MRL	< MRL	0.7	3.5	23,000	Urban
572	2.80	< MRL	< MRL	< MRL	< MRL	2.2	Shallow Aquifers
749	1.07	< MRL	< MRL	< MRL	< MRL	1.3	Agricultural

Notes: MRL-Method Reporting Limit
Data compiled from 75 separate studies/1,625 samples.
Benzene detection frequency was 4.93 for the urban wells.
79 percent of Denver urban wells affected, 37 percent for New England and Harrisburg, PA.

Sideline: California DHS reports 1.2 percent of 2,000 drinking water sources had detectable levels of MTBE in 1997. Five sources were over 35 µg/L.

Exhibit 2. Maximum Concentration of MTBE in a Given Quarter, 1997, Orange County, California



site calculated from the quarterly monitoring data from 1997. It is clear that the largest variability is between 50 and 1,000 µg/L, which tells us the most significant sources of MTBE are greater than 1,000 µg/L and the variability of MTBE in the range of 50 to 1,000 µg/L is large. One possible explanation for the higher variability is the proximity of the monitoring wells to the actual source of MTBE at some sites.

Exhibit 5 illustrates the seasonal variability of MTBE by presenting the average 50th percentile of the maximum MTBE concentrations for all of the sites for 1997. There is a rise in the average maximum concentration in the third and fourth quarters. The clean fuels program in the State of California mandates 11 percent MTBE by volume in gasoline during the summer months and we see this in the wells in the months that follow.

Exhibit 3. 1997 Exceedence Distribution for Maximum MTBE Concentration at a Service Station Site, Orange County, California

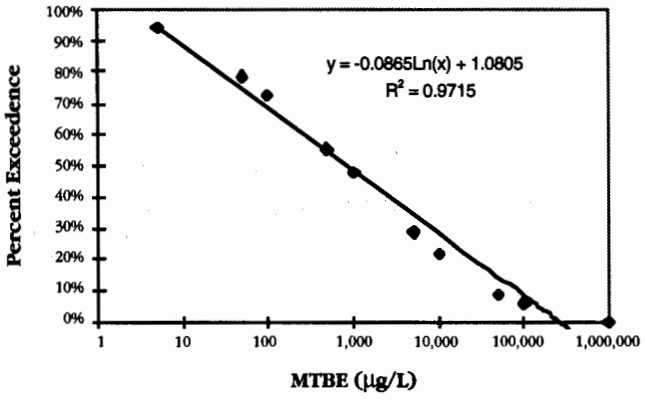
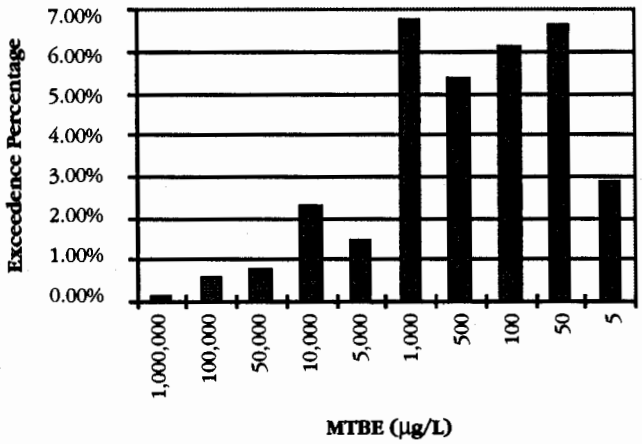


Exhibit 4. Variation Percentage for 1997 Based on Quarterly Data, Orange County, California



FAR FIELD MTBE GROUNDWATER OBSERVATIONS

There are three detailed field studies of MTBE that have been conducted in recent years, which will be examined in some detail in this article. First, and probably the most famous, is the case study of the MTBE contamination of the City of Santa Monica, California's drinking water supply. **Exhibit 6** shows some of the MTBE-related statistics on the Santa Monica plume(s) obtained from Brown et al. (1998). For the approximate groundwater flow rates and the initial average breakthrough concentration of 33.2 µg/L, a 14,100 gallon gasoline tank with a 1 percent loss at an average 5 percent MTBE by volume would account for the mass (ignores

Exhibit 5. 1997 Seasonal Fluctuations for the 50th Percentile Maximum MTBE Concentrations, Orange County, California

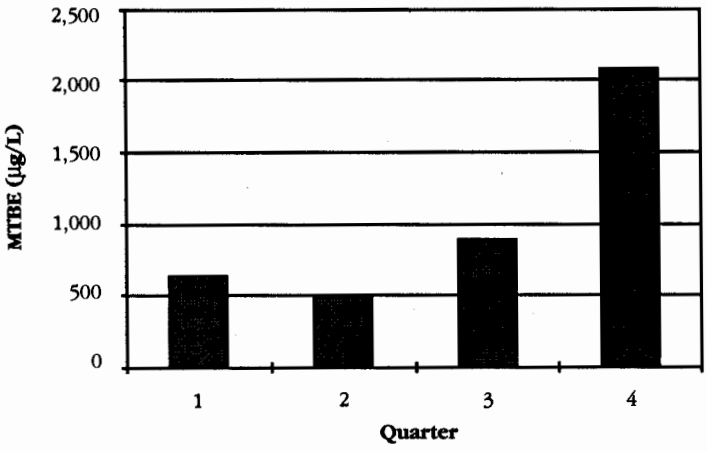


Exhibit 6. Santa Monica Charnock Well Field

- Five municipal extraction wells affected by MTBE. On MWD water indefinitely.
- Average breakthrough/discovery concentration of MTBE=33.2 µg/L.
- Five MGD for one month = 42.4 pounds MTBE recovered.
- At 1 percent loss, 5 percent MTBE initial equates to 14,100 gallons supply.

Average Maximum Concentration of MTBE = 244.5 µg/L at production wells.

advection, dispersion, sorption, and reaction). One of the key questions in Santa Monica was to determine the potential contributors to the problem.

Continuing with our analysis of the Santa Monica MTBE problem, consider what we know about the groundwater plume. **Exhibit 7** summarizes the longitudinal, lateral, and vertical extent of the main MTBE plume in groundwater as well as the main transport theories (data obtained from Brown et al., 1998). Traditional groundwater monitoring wells were used in Santa Monica to determine the extent of the plume. Future work planned in the area includes vertical profiling of the MTBE plume and low-flow groundwater sampling techniques (~0.5 L/min and redox equilibrium). The actual length of the MTBE varies depending on the initial source location; the minimum length is reported in Exhibit 7. The main transport theory in Santa Monica is the vertical migration of the MTBE plume through an uppermost aquitard located approximately 50 feet below the groundwater table surface of the uppermost aquifer.

The second MTBE site we will examine is located in North Carolina and the research was performed under the direction of Dr. Robert Borden of North Carolina State University. **Exhibit 8** provides a summary of the length statistics and transport theories from a continuous source of MTBE from a leaking underground storage tank (data obtained from Borden et

Exhibit 7. Santa Monica Charnock Plume(s)

- At least 1200 ft in length.
- Approximately 50 ft to 150 ft wide.
- Varies from 10 to ? ft in thickness.

As many as 26 sources, the major contributors have settled or are close to settling.

Main Transport Theories

A. Aquitard High-Permeability Window.
B. Monitoring Well Cross-Connection.
C. Poorly Abandoned Water Wells.

al., 1997). A series of four groundwater monitoring well "fences" were located at 36m, 88m, and 177m downgradient of the source. In addition, the vertical extent of the plume was monitored at each of these fence locations with a series of short vertical well screens at varying distances below the water table (to a maximum depth of 28 feet). The leading edge of the groundwater plume is approximately 700 to 800 feet downgradient from the leaking tank. The source release rate of MTBE is approximately 2 grams per day or 3.1 pounds during the 700-day study period. The infiltration rate (pluming plume) combined with possible transport through the underlying aquitard are the primary mechanisms for mass loss between downgradient transects.

The third and final detailed analysis of an MTBE is a study conducted by the University of Waterloo at Base Borden, Ontario, Canada. An initial mass of 1.66 pounds of MTBE was injected approximately 5 feet below the water table, which resulted in a plume size summarized in **Exhibit 9** (data obtained from Schirmer et al., 1997 and Bauman, 1997). Once again, a series of short-screen monitoring wells (piezometers) were installed vertically and areally downgradient of the plume. The main conclusion after the initial three-year study was that no biodegradation of MTBE took place in the aquifer. After seven to eight years after the initial injection, the project team decided to try to find the remaining MTBE mass in the shallow aquifer. The conclusion of the search after seven to eight years by some is intrinsic biodegradation due to the lack of mass of MTBE discovered in the projected region of the plume. Others speculate that hydrodynamic dispersion and heterogeneities in the forested region were the primary mechanisms of transport. Our opinion is shared by the latter school of thought. There is no real evidence of biodegradation of the MTBE plume other than the lack of mass detected in geoprobe samples seven to eight years after initial injection.

In summary, there are two major questions that must be asked to help

Exhibit 8. North Carolina State University (Borden)

- At least 580 ft in length, leading edge estimated to be approximately 700 to 800 ft.
- Approximately 250 ft wide.
- At least 28 ft in thickness (to top of clay aquitard). Possible MTBE in aquitard (personal communication). Large infiltration/recharge suspected mechanism for vertical migration.

One main continuous source area, fully characterized. Release rate of approximately 2 grams per day over the study period (700 days, 1,400 grams or 3.08 pounds).

Main Transport Theories

A. Some degradation at source area.
B. No evidence of decay downgradient from source.
C. Possible accumulation/leakage in/through lower aquitard.

Exhibit 9. Waterloo MTBE Study, Borden Aquifer, Ontario, Canada

- At least 800 ft to 1000 ft from source after 3000 days from injection. Approximate longitudinal length of the plume was 165 ft.
- Approximately 150 ft wide.
- At least 15 to 20 ft in thickness (to top of aquitard). MTBE distribution confined to the top of the aquitard at the 2,700-3,000 day sampling events.

Instantaneous source injected 5 ft below the water table. Approximately 753 grams or 1.66 pounds of MTBE.

Main Transport Theories

A. Travel along top of aquitard after 7-8 years.
B. No TBA (tert-Butyl Alcohol) or TBF (tert-Butyl Formate) found after 7 years.
C. Intrinsic biodegradation? Not really supported.

clear up the intrinsic biodegradability of MTBE. First, are there any laboratory results that mimic field conditions where the biodegradability of MTBE is examined? Second, if there is significant biodegradability of MTBE in aquifers, why is the average length of MTBE plumes in our three studies approaching 1,000 feet (all three studies were conducted in sandy aquifers with an underlying aquitard 20 to 50 feet below the water table)? We will take a look at these questions in the next section.

SUMMARY OF MTBE MICROCOSM STUDIES

Since 1984, researchers have conducted numerous microcosm studies on MTBE biodegradability. A summary of the significant microcosm studies reported in the literature is given in **Exhibit 10**. From 1984 through 1993, MTBE was found to be recalcitrant to both aerobic and anaerobic biodegradation conditions. There was limited biodegradation of MTBE reported by Mormile et al. (1994) and Yeh and Novak (1994) under denitrifying conditions and biodegradation evidence using isolated strains under nitrifying conditions by Salinitro et al. (1994). Borden et al.(1997) and Schirmer et al. (1997) both reported a 50 percent reduction of MTBE under aerobic conditions using native (perhaps naturally adapted?) bacteria from an MTBE-affected aquifer. The Coast Guard (USEPA, 1997) reported MTBE degradation under methanogenic conditions and Envirogen (1998) reported some MTBE degradation using a propane substrate. The products TBA (tert-Butyl Alcohol) and TBF (tert-Butyl Formate) of MTBE biodegradation were not found in any of the studies summarized in Exhibit 10. It is quite apparent that more laboratory and field research is necessary to determine the rate, existence, and pathways of MTBE biodegradation.

SUMMARY OF FIELD STUDIES

In closing, the field data presented earlier are summarized in **Exhibit 11**.

Exhibit 10. MTBE Microcosm Studies

1984—Fujiwara et al. Recalcitrant. Aerobic.
1985—Novak et al. Recalcitrant. Aerobic.
1990—Jenson/Arvin. Recalcitrant. Aerobic.
1990—Barker et al. Recalcitrant. Aerobic.
1993—Suflita/Mormile. No degradation. Anaerobic.
1994—Salinitro et al. Isolated strain. Aerobic(nit).
1994—Mormile et al. Limited degradation. Anaerobic(dn).
1994—Yeh/Novak. Recalcitrant. Anaerobic(dn).
1995—Horan/Brown. Slight, < O2, > CO2. Aerobic.
1997—Borden et al. 50 percent reduction 2-1 mg/L. Aerobic.
1997—Schirmer et al. 50 percent reduction 2-1 mg/L. Aerobic.
1997—Bovard/Baker. No degradation. Aerobic.
1998—Coast Guard NC. Extensive. Methanogenic (USEPA, 1997).
1998—Envirogen. Some degradation. Propane substrate (Borden, 1998).
1998—LA County. Some removal. Aerobic/fixed-film (Borden 1998).

TBA and TBF products seemingly difficult to find.

One additional site from Long Island, New York was added to the table (Weaver et al., 1996) for the sake of completeness. There are two columns pertaining to longitudinal distance. The first is the actual length of the plume. For the instantaneous injection (Waterloo) or the removal of the source (New York), the length (longitudinal extent) of the plume is not measured from the initial source location. The second is the overall distance traveled by the plume. The last column in the table is the estimated mass of release or the mass of MTBE within the aquifer.

CONCLUSIONS

There is some evidence to support limited aerobic and anaerobic biodegradation of MTBE via microcosm studies conducted under both aerobic and anaerobic conditions. In this article, we provided summaries and discussed regional, near field, and far field MTBE concentration data in aquifers across North America. MTBE emanating from underground gasoline storage tanks can easily travel over 1,000 feet downgradient from its source and there are reports of MTBE traveling as far as three miles from a source in groundwater. In the studies examined in some detail in this article there is no definite evidence that MTBE biodegrades intrinsically. Data from Orange County, California indicate 77.3 percent of the sites had a maximum MTBE concentration of at least 35 µg/L and 48.3 percent for 1,000 µg/L. Data from Orange County also indicate a rise in MTBE concentrations in aquifers in the fall and winter just after the peak MTBE usage period in the summer months. In summary, MTBE is setting travel distance records in groundwater across the country, seems resistant to

Exhibit 11. Summary of Significant MTBE Field Studies

Site	*Length*	*Distance Traveled*	*Width*	*Depth*	*Mass*
SM	1,200	1,200 (min)	50-150	10-?	42 lbs/mo (rate of release)
NC	700-800	700-800	250	28	3.0 lbs (released in 700 days)
Wat	165	800-1,000	150	15-20	1.7 lbs (instantaneous)
+ NY	3,000	4,500	NR	20-80	850 lbs (within plume)

All lengths in feet
NR=Not Reported
+NY= E. Patchogue, New York. Weaver et al., 1996.

biodegradation, and appears to persist in the subsurface environment. Once MTBE enters an aquifer, its primary means of travel is through the path of least resistance (with the flow) and there is evidence to suggest its vertical migration is enhanced by infiltration.

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