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**MTBE RELEASES INTO THE ENVIRONMENT  
AND THEIR POTENTIAL FOR OCCURRENCE IN  
WATER SUPPLIES**

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**THIS COMPLETE REPORT CONTAINS ALL PERTINENT APPENDICES  
AND IS AVAILABLE FOR DISTRIBUTION.**

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## ABSTRACT

Methyl tertiary butyl ether (MTBE) is an oxygen-containing gasoline blending component used throughout the world fuel markets to enhance the octane of gasoline and more recently in the U.S. to making cleaner burning gasolines. MTBE accomplishes this by simultaneously substituting for some of the high octane aromatic compounds in gasoline and adding oxygen to improve combustion. Though originally introduced into the U.S. market in 1979, its production capacity has been growing nearly 20 percent or more per year in the past decade to a point where it is now used in approximately 30 percent of the U.S. gasoline and represents nearly 4 percent of the total gasoline volume.

Because of MTBE's growing wide-spread use, it is beginning to show up in the environment, both air and water, at detectable levels. Like other gasoline related VOCs (volatile organic compounds), it also oxidizes away in the atmosphere. Though it is biodegradable under waste water treatment conditions, it has shown little tendency to readily biodegrade in the subsurface. This has led to a concern that it may some how build up in the ground water or drinking water supplies to unhealthy concentration levels.

The amount of MTBE escaping into the environment is expected to peak in the mid-1990s at a little over 200 million pounds per year (90,720,000 kg/yr). Very little of this (< 1 million lbs. (453,600 kg)) has the probability of getting into the ground-water system. The amount of MTBE released into the environment will begin decreasing as VOC emissions from the car fleet are reduced with fleet turnover, and as underground storage tank (UST) leaks are minimized when federal regulations for USTs are fully implemented. Total MTBE releases are expected to drop to nearly half the 1995 amounts by the year 2010.

The causes, trends, patterns, and typical concentrations of MTBE-impacted ground water are well understood, and are defined in this report by MTBE analyses of ground-water samples from over 5,350 wells and springs. Contrary to early field reports, recent research has shown that dissolved-phase MTBE does not cause co-solvency of aromatic hydrocarbons in ground water, but rather MTBE's presence in gasoline reduces aromatic concentrations in the ground water. Recent fate and transport studies have also shown that MTBE does not inhibit the natural, beneficial, aerobic biodegradation of aromatic hydrocarbons like benzene, toluene, ethylbenzene, and xylenes (BTEX). No process exists by which MTBE concentrations can "build-up" or accumulate in the ground water to concentrations greater than the incoming source. MTBE plumes from blended gasoline spills are typically 1.5 to 2.0 times larger than the associated BTEX plumes due to retardation rate differences and to the natural attenuation of BTEX compounds.

In March 1995 the United States Geological Survey (USGS) announced results from a national ground-water assessment program. Dissolved-phase MTBE was detected in 27% percent of ground-water samples collected from shallow, urban wells and springs. Nationwide, MTBE was the second most commonly detected compound. Initially this data caused concern that MTBE was ubiquitously impacting ground water. However, a careful review of the sampling program and the analytical data revealed:

- Nationwide, MTBE concentrations averaged 0.6  $\mu\text{g/L}$
- Nationwide, 6 of 211 (3%) shallow, urban wells exceeded 20  $\mu\text{g/L}$  of MTBE; 3 of 211 (1.5%) exceeded 200  $\mu\text{g/L}$  of MTBE
- Nationwide, 4 of 413 (1.0%) deeper wells more representative of most drinking water aquifers contained MTBE, and none were higher than 1.3  $\mu\text{g/L}$
- High MTBE concentrations were associated with BTEX occurrence and low dissolved oxygen, and thus were likely attributable to local point source releases of MTBE-blended gasoline (ex. USTs)
- Well selection methods appear to slightly bias the results towards discovering MTBE from these local point sources

The work presented here suggests that background equilibrium levels of MTBE in the environment will be limited to concentration levels less than 2 ppbv in the atmosphere and 2  $\mu\text{g/L}$  in water (wet precipitation, surface water, ground water). Local spills of MTBE-blended gasoline (and in rare cases pure MTBE or MTBE-impacted tank bottom waters) may lead to localized MTBE concentrations in ground water that exceed regulatory levels for water consumption. While some public and private wells may have MTBE at concentrations above health standards, factors like low odor and taste detection thresholds help prevent water consumption from such wells. Many of the existing clean-up methods used for gasoline aromatics can also be used to remediate MTBE. However, remediating the MTBE portion of a blended gasoline ground-water plume typically costs 2.6 to 3.1 times as much as remediating the BTEX portion of the plume.

*Authors' Note: The various sections in this paper have been have been written separately by the individual authors, and have been identified by the author's initials after the section title.*

## INTRODUCTION (WJP & JMD)

Though MTBE has been commercially used in Europe since 1973, U.S. production began in 1979 to use MTBE as one of the octane replacements for lead compounds and as an alternative to aromatics for raising octane ratings in gasoline. MTBE's use as an oxygen additive began in Colorado in the winter of 1988. MTBE now supplies most of oxygen in reformulated gasoline used in ozone non-attainment areas (oxygen in gasoline was required by the 1990 Clean Air Act). These non-attainment areas are generally found around metropolitan centers with high population densities.

Many of the VOCs (volatile organic compounds) released into the environment are associated with the use of gasoline in vehicles. Not only do these VOCs contribute to ozone production in the summer time, but they are a significant source of toxic compounds such as benzene. A main environmental benefit of using MTBE is that it replaces aromatics such as benzene in gasoline which thereby helps reduce the amount of benzene released into the environment when the gasoline escapes from the fuel distribution systems and vehicles.

In almost all respects, MTBE and benzene from gasoline will follow similar pathways in the environment. MTBE and benzene will both generally volatilize into the air, but benzene will be more persistent in the atmosphere since it doesn't oxidize as easily as MTBE. Since MTBE is also partially water soluble, it will also enter water supplies through either rain, spills or leaking underground storage tanks in much the way that benzene does. However, MTBE is not nearly as biodegradable as benzene in nature and will be more persistent in the water phase as a result. Therefore, MTBE in the water is expected to disappear from water mainly by volatilizing back into the atmosphere where it is then oxidized. The net result of MTBE's use in gasoline is an increase of MTBE in the environment but a decrease of benzene.

Several early works reported MTBE contamination of ground water and drinking water (1, 2). In addition, they raised concerns about how the presence of MTBE may complicate or worsen contamination by the hydrocarbons. Concerns regarding MTBE fate and transport were increased in 1995 due to a national ground-water assessment by the United States Geological Survey (USGS) that found MTBE in shallow monitoring wells more frequently than many other contaminants.

## PURPOSE (WJP & JMD)

The purpose of this report is to present a full analysis of MTBE releases into the environment including:

- the sources of MTBE releases to the environment and the concentrations created by them
- how MTBE transfers from one media to another (ex: surface water to atmosphere)
- subsurface fate and transport of MTBE
- what MTBE concentrations are expected in various media (atmosphere, wet precipitation, surface water, ground water)
- initial estimates of MTBE in the nation's drinking water supply

In this paper equilibrium data and various models were used to estimate MTBE concentrations and transfers in the environment. Measured MTBE concentrations and mass loadings are provided where available. In most cases, the estimation techniques used identify the upper bounds on the amount of MTBE that may be transferring between the various environmental compartments, or estimate the highest MTBE concentrations possible in a media.

This paper reviews recent research and field experience to update the reader on the current knowledge about MTBE fate and transport and how it affects subsurface movement of aromatic hydrocarbons. Additionally, it presents the findings of the USGS and reviews the data significance. These results are compared with data about MTBE occurrence in drinking-water supplies. Finally, the methods and costs of remediating MTBE ground-water plumes are addressed.



## MTBE USAGE (WJP & DJB)

MTBE was originally developed as an octane enhancer in gasoline. Its use is almost exclusively limited to gasoline blending. Because of MTBE's favorable octane in gasoline, its use has grown at nearly 20 percent or more per year for the past decade. Table 1 provides an estimate of MTBE's historical and projected use in U.S. gasoline.

	Thousands of barrels per day (M B/D)	Millions of gallons /yr (MM gal/yr)	Typical blending percent in gasoline	Percent of gasoline containing MTBE	MTBE Volume percent of all gasoline
1980	12	190	4 %	4 %	0.2 %
1985	35	540	5 %	10 %	0.5 %
1990	90	1380	7 %	18 %	1.3 %
1995	250	3830	12 %	29 %	3.5 %
2000	280	4290	11.5 %	33 %	3.8 %
2005 -	300	4590	10.5 %	37 %	3.9 %

Source: ARCO Chemical Company (Reference 3)

## MTBE USE IN GASOLINE (RARI)

MTBE use as a gasoline additive has increased in three stages over the past 15-20 years. First, MTBE was used in the early and mid-1980s as a high octane replacement for lead as lead was being phased out of leaded gasoline and as unleaded gasoline was gaining an increasing market share. Second, beginning in the late 1980s, MTBE was the primary oxygenate used in winter gasoline to reduce CO emissions in areas with high ambient CO levels. This oxygenated gasoline is commonly called *oxyfuel*. When MTBE is used in oxyfuel, its concentration is roughly 15 percent by volume (vol%). Oxyfuel only tends to be used in the coldest 4-5 months of the winter. Third, beginning in 1995, MTBE was again the primary oxygenate used in reformulated gasoline (RFG), a gasoline designed to reduce both VOC and toxics emissions in high ozone areas. When MTBE is used in RFG, its concentration tends to be about 11 vol%. The RFG oxygenate requirement, unlike that of oxyfuel, applies year-round. When MTBE is not used in either oxyfuel or RFG, ethanol tends to be the oxygenate of choice.

Today, the bulk of MTBE use is in oxyfuel and RFG. RFG represents about 30% of all U.S. gasoline when factoring in recent opt-outs by the Governors of Wisconsin, Maine and Pennsylvania (4). Beginning with 1996, California Phase II RFG must be sold in the entire state of California. While this fuel is not required to contain 2.0 weight percentage (wt%) oxygen outside of the winter months, it is likely that it will contain substantial amounts of oxygenate. For the purposes of this analysis, it will be assumed to contain the 2.0 wt% oxygen required in federal RFG. The addition of the rest of California in 1996 (Los Angeles and San Diego received federal RFG in 1995) would increase the RFG fraction of U.S. fuel consumption to 35.2%.

Oxyfuel represents about 29.1% of winter fuel consumption. Because the oxyfuel program varies in length from year-round in Minneapolis-St. Paul to four months in most areas, oxyfuel represents 12.4% of annual U.S. gasoline consumption.<sup>1</sup> However, about 22.2% of winter fuel and 9.4% of annual U.S. gasoline consumption must meet the requirements of both programs.<sup>2</sup> Thus, overall, starting in 1996, about 25.8% of annual U.S. gasoline will have to meet only the RFG requirements, 9.4% will have to meet both RFG and oxyfuel requirements and 3.0% will have to meet the oxyfuel requirements.

MTBE is estimated to be the oxygenate used in about 80% of RFG and RFG/oxyfuel, and about 50% of oxyfuel. When present, MTBE represents approximately 11.5 vol% of RFG and 15 vol% of RFG/oxyfuel and oxyfuel. Thus, overall, MTBE represents roughly 3.7 vol% of all U.S. gasoline in 1996.

This increased use of MTBE in gasoline has raised a number of potential health concerns. One of these concerns is the possible contamination of drinking water by MTBE through the transfer of MTBE in ambient air to the ground by rain. This transfer of MTBE from air to rain will depend directly on the ambient concentration of MTBE over wide geographical areas. The purpose of this section is to project these ambient concentrations.

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<sup>1</sup> EPA estimated this figure to be 17% in early 1993. However, this was prior to the change in the New York City program from year-round to winter only and the reduction in the oxygen content of oxyfuel in Los Angeles from 2.7 to 2.0 wt% (5). These changes are estimated to reduce oxyfuel use by 3% of annual U.S. gasoline consumption.

<sup>2</sup> Again, EPA's estimate was reduced by 3% due to changes in the oxyfuel program since the time of its projections (see previous footnote.)

The breakdown of MTBE and ethanol use in oxyfuel and RFG varies dramatically from city to city and can vary from year to year, as well. Either MTBE or ethanol can represent 100% of the oxygenate used in a given city during a specific year. Rather than calculate MTBE emissions for the average U.S. city which may not apply to any city in particular, this analysis will assume that MTBE is used in 100% of the oxyfuel or RFG being used in a city. This will be representative of those cities where MTBE dominates the oxygenate market, which is the worst case scenario for the ambient MTBE concentrations and thus potential transfer of ambient MTBE into wet precipitation. The projections developed herein will then be conservative for those cities where ethanol has a significant or dominant market share. Finally, MTBE use outside of both oxyfuel and RFG is roughly an order of magnitude lower than in these two low emission fuels (e.g., less than 1-2 vol%). Thus, the projections developed herein will be roughly an order of magnitude greater than those likely to exist in cities not participating in either of these two programs. In summary, the projections developed here will be worst-case scenarios for high MTBE use areas, and will greatly overestimate MTBE concentrations in the atmosphere and water in low MTBE use areas.

## MTBE RELEASES INTO ENVIRONMENT (WJP & OJB)

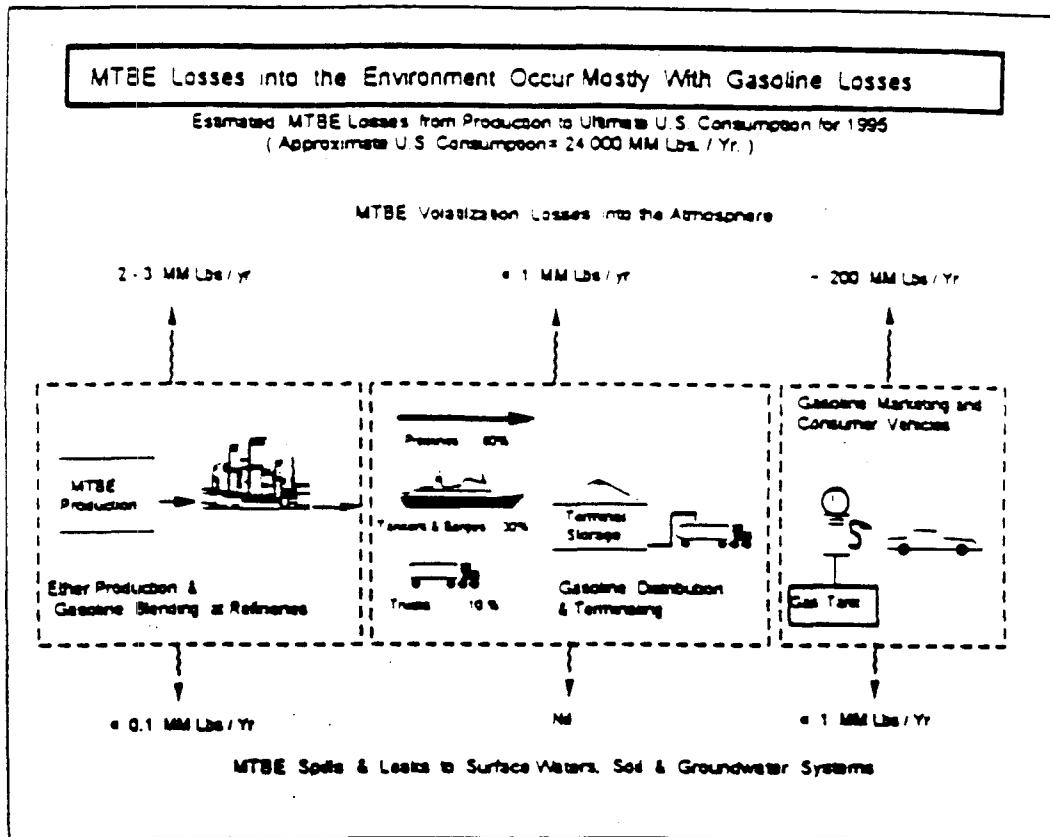
MTBE is manufactured by chemically combining methanol with isobutylene. Its volatility and other handling properties are similar to that of gasoline. In almost all cases, it is transported and stored much the same as gasoline. Some of the MTBE is made in the petroleum refineries, but most is manufactured at chemical facilities and then transported to the refineries where it is blended into gasoline. The MTBE-containing gasoline is then transported to the distribution terminals (via pipelines or other methods) where it is distributed to the USTs at gasoline service stations for sale to consumers.

From initial production to the ultimate consumption in the vehicle's engine, there are numerous points for MTBE to escape into the environment. The releases and pathways through the environment for MTBE will generally parallel those for the other gasoline VOCs, particularly benzene. Because of MTBE's relatively high volatility, most of it will tend to go into the atmosphere where it is expected to ultimately oxidize to carbon dioxide and water (similar to other VOCs).

The estimated releases for MTBE along its distribution steps to the consumer can be illustrated for 1995 in Figure 1. The releases between its production and gasoline blending are reported under EPA's Toxic releases inventories and have been ratioed up from 1992 to 1995 by using MTBE annual consumption numbers (Table 1). The releases from the other transfer steps are estimated in other sections of this paper.

Some observations can be made from this illustration. The vast majority of MTBE losses into the environment are via gasoline losses. The location for most MTBE releases (98 + %) into the environment are going to occur in the consumer marketplace, and not at industry locations or bulk gasoline distributions. For comparison, about 85% of the benzene releases are from mobile sources. Also, the vast majority of MTBE releases (99 + %) will initially go into the atmosphere and not into the water or soil. Again, this seems to be consistent with general VOC losses associated with gasoline.

Figure 1



PHYSICAL AND CHEMICAL PROPERTIES OF MTBE (WJP & OJB)

To understand MTBE's movement in the environment, it is first necessary to tabulate MTBE's properties. Most of the relevant properties are listed in Tables 2A & 2B

Table 2A Information and properties for MTBE		
Synonyms	methyl tertiary-butyl ether 2-Methoxy-2-methyl propane methyl-1, 1-dimethylethyl ether tertiary-butyl methyl ether	References
CAS No.	1634-04-4	6
Chemical Formula	C <sub>5</sub> H <sub>10</sub> O	6
Molecular Weight	88.13	6
Physical State	Colorless Liquid	6
Boiling Point	55.2° C	6
Melting Point	-109° C	5
Density @ 25 ° C	0.735	6
Log Kow @ 25 ° C	1.23	3
Odor Detection Threshold in Water (µg /L)	45	7
Odor Detection Threshold in Air (ppbv)	53, 100	7, 8
Taste Detection Threshold in Water (µg /L)	39	7
Odor Characteristics	Terpene like, ether alcohol	3, 7
Conversion Factor	1 ppbv = 3.804 µg / m <sup>3</sup> (air)	

Table 28  
Temperature Sensitive Properties of MTBE

Temperature (°C)	0	20	25	40	References
Density (g/ml)	0.781	0.7405	0.7350	0.719	8
Vapor Pressure (mm Hg)	79	202	250	449	8
Solubility in water (mass %)	8.3	4.2	3.6	2.5	9
Solubility in salt water (mass %)	NM	NM	3.78	NM	3
Henry's Law Constant (atm m <sup>3</sup> / mol)	$6.25 \times 10^{-4}$	$4.25 \times 10^{-4}$	$6.59 \times 10^{-4}$	$2.26 \times 10^{-3}$	10
Log K <sub>ow</sub> (octanol/water) (predicted except for 25 °C)	0.96	1.18	1.23	1.35	3, 11
K <sub>oc</sub> (octanol/carbon) (predicted)	5.5	9.0	10.2	13.5	11
Log BCF (predicted) (Bio Concentration Factor)	0.12	0.3	0.35	0.45	11

## MTBE EMISSIONS FROM OXYFUEL AND RFG (RAR)

A three-step process was used to estimate the emissions of MTBE from oxyfuel and RFG. First, VOC emissions from these fuels were estimated. Second, the MTBE fraction of these VOC emissions were estimated. Third, the MTBE fractions were applied to the VOC emission estimates to develop estimated MTBE emissions. This approach was taken, rather than directly developing estimates of MTBE emissions, because of the relative amounts of data are available describing both VOC and MTBE emissions. Tens of thousands of tests have been performed to estimate VOC emissions under a wide variety of ambient conditions and for varying degrees of vehicle maintenance. Sophisticated models, such as EPA's MOBILE model and California's EMFAC model, have been developed to convert this data into estimates of fleet-wide emissions. In contrast, very few of these tests included measurements of MTBE emissions. At the same time, the MTBE fraction of VOC emissions is not expected to change as dramatically between vehicles or operating conditions as do absolute VOC or MTBE emissions. Therefore, starting with the best estimate of in-use VOC emissions possible allows the wealth of emission testing to be used to the fullest extent possible. The relatively smaller database of MTBE measurements is used to estimate the portion of the overall mass emission equation which is most consistent. Together, this approach provides the most accurate estimate of in-use MTBE emissions possible.

### VOC Emissions from Oxyfuel and RFG

Baseline VOC emissions were estimated using EPA's MOBILE5a model for calendar years 1995, 2000, 2005, and 2010. As MTBE presumably can dissolve into wet precipitation throughout the summer and winter, average summer and winter temperatures were used in lieu of high ozone temperatures which are often used in urban air quality analyses. The daily low and high temperatures of 66.8 and 87.2°F for the summer and 39 and 57°F for the winter, respectively were taken from previous EPA analyses (12, 4).

While RFG can be modeled directly using MOBILE5a, this was not done here. The effect of RFG on exhaust emissions contained in MOBILE5a precedes the final complex model developed by EPA for RFG certification, as MOBILE5 was developed in 1992 and the final complex model was not completed until December of 1993 (MOBILE5a is only a corrected version of MOBILE5; it does not contain any fundamentally different emission projections). Thus, MOBILE5a was run without RFG present and the complex model was used to project the change in exhaust emissions between RFG and Clean Air Act (CAA) baseline gasoline<sup>3</sup>, which is the default fuel in MOBILE5a (13).

MOBILE5a was used directly to model the emission effects of oxyfuel. An oxyfuel containing 2.7 weight percent oxygen in the form of MTBE was assumed in the modeling.

The portion of EPA's complex model which addresses non-exhaust VOC emissions is based solely on the effect of the fuel's Reid Vapor Pressure (RVP) and was developed directly from MOBILE5a output (4). However, the temperatures assumed in the modeling performed to develop

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<sup>3</sup> Section 211(k) of the CAA, as amended in 1990, defines the summer baseline gasoline for the reformulated gasoline program. This composition of this fuel is very near that of average summer gasoline in 1990, as determined by national fuel surveys. As ozone is primarily a summer concern, this fuel is often commonly referred to as CAA baseline gasoline.



the complex model are representative of high ozone days. Thus, MOBILE5a was used directly here to project non-exhaust emissions with RFG. Both sets of temperatures described above are representative of the nation as a whole. Winter RFG must meet the same requirements regardless of where it is sold. However, summer RFG differs geographically. During Phase 1 (i.e., 1995-99), RFG sold in southern cities must meet a lower RVP standard (7.1 pounds per square inch, or psi, on average) than that sold in the north (8.0 psi on average) (4). Thus, before running MOBILE5a for 1995, a single average RVP for RFG was developed by assuming that 40% of RFG met the 7.1 RVP standard and 60% of RFG met the 8.0 RVP standard. The result was an average RVP of 7.6 psi.

In Phase 2, the RVP of RFG will tend to be approximately 6.7 psi in both the north and the south (4). Thus, a single RVP of 6.7 psi was used in the 2000, 2005, and 2010 MOBILE5a modeling. The results of the MOBILE5a modeling is shown below.

Table 3			
VOC Emissions From Motor Vehicles (g/mi)			
MOBILE5a			
Calendar Year /Emission Type	Average Commercial Fuel		Oxyfuel
	Summer	Winter	Winter
1995			
Exhaust	1.761	2.509	2.22
Evaporative	0.565	—	—
Refueling	0.044	0.049	0.049
Total	2.37	2.558	2.269
2000			
Exhaust	1.301	1.831	1.609
Evaporative	0.279	—	—
Refueling	0.032	0.04	0.04
Total	1.612	1.871	1.649
2005			
Exhaust	1.12	1.561	1.368
Evaporative	0.18	—	—
Refueling	0.023	0.028	0.028
Total	1.323	1.589	1.396
2010			
Exhaust	1.054	1.455	1.278
Evaporative	0.132	—	—
Refueling	0.019	0.023	0.023
Total	1.205	1.478	1.301

As mentioned above, the great majority of MTBE is used in RFG and oxyfuel. Areas receiving these fuels tend to also have both enhanced I/M and Stage II refueling controls. Thus, MOBILE5a was run assuming both of these programs were in place. Vehicle speed was assumed to be 19.6 mph (31.5 km per hour), consistent with EPA regulatory analyses (4, 5, 12). The MOBILE5a input file for the three scenarios and four calendar years are shown in Appendix A.

In order to use the Complex Model, one must estimate a wide variety of gasoline properties. When developing the RFG program, EPA projected the composition of RFG with MTBE and ethanol. These compositions were based on refinery modeling and technical judgment. However, given the fact that RFG has now been sold for eight months, actual fuel survey data is now available and provides a much more accurate estimate of the composition of RFG.

The American Automobile Manufacturers Association (AAMA) conducts a survey of gasoline quality each January and July. The July 1995 samples have already been taken, but the results will not be available until late 1995. To obtain similar data earlier ARCO contracted with Core Laboratories (which also conducts the AAMA survey) to collect and analyze the composition of RFG in five RFG cities during the summer of 1995 (ARCO Chemical Company). The results of this survey for Dallas, Chicago, Los Angeles, New York, and Philadelphia are shown in Table 4.

	1990-91 (Phase I RVP)	1992-94 (Phase II RVP)	1995 (RFG)
MTBE (wt% oxygen)	0.3	0.3	1.7
MTBE (vol%)	1.4	1.6	9.5
Ethanol (wt% oxygen)	0.2	0.3	0.4
Ethanol (vol%)	0.4	0.8	1.1
Sulfur (ppm)	313.0	309.3	291.0
RVP (psi)	8.4	8.0	7.7
E200 (Vol%)	43.1	42.9	49.4
E300 (Vol%)	80.7	80.5	81.8
Aromatics (Vol%)	29.7	30.0	26.0
Olefins (Vol%)	10.4	12.0	9.6
Benzene (Vol%)	1.30	1.27	0.70

The results of the winter 1995 AAMA fuel survey for seven cities receiving RFG (the five cities mentioned above plus Boston and Washington, D.C.) are shown in Table 5.

Table 5			
Fuel Survey Results from 7 Cities			
Winter 1995 AAMA Fuel Survey			
	1990-92 Pre-Oxyfuel	1993-94 Oxyfuel	1995 RFG
MTBE (wt% oxygen)	0.2	1.5	2
MTBE (vol%)	0	0	0
Ethanol (wt% oxygen)	0.2	0.3	0.3
Ethanol (vol%)	0.4	0.8	0.8
Sulfur (ppm)	277	314	243
RVP (psi)	13	12.9	12.3
E200 (Vol%)	49.6	54.3	57.3
E300 (Vol%)	82.8	82.8	84
Aromatics (Vol%)	26.3	24.8	20.6
Olefins (Vol%)	10.7	12	9.6
Benzene (Vol%)	1.60	0.95	0.60

These surveys allow the direct determination of the impact of MTBE use on non-controlled fuel parameters such as sulfur, olefins, and T90, which can have a significant effect on emissions. As can be seen, about 20% of the oxygen in the summer RFG in the five cities was supplied by ethanol, 80% by MTBE. In-use, refiners will almost never mix MTBE and ethanol. Refiners will almost always use one or the other. Due to the differential oxygen content of MTBE and ethanol, less volume of ethanol is needed to meet the 2.0/2.1 weight percent oxygen requirements than of MTBE. Thus, MTBE provides greater dilution (11.6 vol% versus 6.1 vol% at 2.1 wt% oxygen) and thus, more total octane than ethanol. In general, this means that other things being equal (i.e., the same refiner, crude oil source, etc.), MTBE RFG blends will show lower levels of sulfur and olefins. Based on the fact that the RFGs surveyed overachieve the RFG toxics and benzene requirements, MTBE blends also likely will show lower levels of aromatics and benzene, as well. These differences mean that MTBE blends will generally produce lower levels of VOC exhaust emissions than ethanol blends.

It was assumed here that the decrease in aromatics, benzene, sulfur and olefins observed was proportional to the volume of oxygenate used. The total volume of oxygenate was determined to be 10.6 and 11.9 vol% in the surveyed summer and winter RFGs, respectively. The percentage change in the gasoline properties for MTBE (at 11.65 vol%), would therefore be slightly greater than indicated by the surveyed summer fuel (by the ratio of 11.65 to 10.6) and slightly less than indicated by the surveyed winter fuel (by the ratio 11.65/11.9). For ethanol, the percentage change in the gasoline properties would always be less due to the fact that its usage level of 5.8 vol% is always less than the total oxygenate volume found in the surveys.

As the pre-RFG gasoline samples in these cities do not match the baseline gasoline contained in the Complex Model (which for summer fuel is specified in the Clean Air Act (CAA)), the effect of RFG on the various fuel parameters indicated by the survey were applied multiplicatively to baseline gasoline to develop an MTBE blend composition consistent with the baseline assumed by EPA in the complex model. The following sets of properties were developed.

Given the similarity of both northern and southern RFG's effect on exhaust emissions, only northern (EPA Class C) fuel was projected. As mentioned above, the non-exhaust VOC emissions were developed using the average RVP of both southern (Class B) and northern (Class C) RFG.

Fuel Parameter	Summer		Winter	
	1990 Baseline	RFG	1990 Baseline	RFG
MTBE (wt% oxygen)	0	2.0	0	2.0
MTBE (vol%)	0	11.0	0	11.0
Sulfur (ppm)	339	316.3	338	297.4
RVP (psi)	8.7	8	8.7	8.7
E200 (Vol%)	41	47.9	50	57.6
E300 (Vol%)	83	84.5	83	84.1
Aromatics (Vol%)	32	27.3	26.4	20.8
Olefins (Vol%)	13.1	10.4	11.9	10.7
Benzene (Vol%)	1.53	0.77	1.64	0.64

The only difference between the CAA baseline fuel and the in-use baseline fuel is the olefin content. While the summer baseline fuel specified in the CAA was quite representative of average gasoline in all other respects, its olefin level was quite low compared to survey results. EPA used the 13.1 vol% level as the true baseline in its analyses of the in-use emission and economic impacts of RFG.

The olefin difference does not appear in the winter, since the CAA did not specify the winter baseline fuel. EPA developed this baseline directly from in-use fuel survey data. While the average RVP of winter fuel is 11.5 psi, Table 6 shows 8.7 psi, which is actually the summer baseline level. When using EPA's complex model to model winter fuels, 8.7 psi must be used in order to obtain correct estimates. The actual winter baseline RVP of 11.5 psi was used in the MOBILE5a modeling.

The EPA Complex Model projects that summer and winter RFG reduce exhaust VOC emissions by 9.39% and 5.58%, respectively. Applying these effects to the MOBILE5a output produced the following mass emission estimates (Table 7):

Table 7				
VOC Emissions From Motor Vehicles (g/mi)				
MOBILE5a/Complex Model				
Calendar Year/ Emission Type	RFG		RFG/Oxyfuel	Oxyfuel
	Summer	Winter	Winter	Winter
1995				
Exhaust	1.596	2.369	2.22	2.22
Evaporative	0.565	—	—	—
Refueling	0.044	0.049	0.049	0.049
Total	2.205	2.418	2.269	2.269
2000				
Exhaust	1.179	1.729	1.609	1.609
Evaporative	0.279	—	—	—
Refueling	0.032	0.04	0.04	0.04
Total	1.49	1.769	1.649	1.649
2005				
Exhaust	1.015	1.474	1.368	1.368
Evaporative	0.18	—	—	—
Refueling	0.023	0.028	0.028	0.028
Total	1.218	1.502	1.396	1.396
2010				
Exhaust	0.955	1.374	1.278	1.278
Evaporative	0.132	—	—	—
Refueling	0.019	0.023	0.023	0.023
Total	1.106	1.397	1.301	1.301

As can be seen, no evaporative emissions are projected in the winter. While such emissions may exist, no reliable data are available upon which to base any reasonable projections. While MOBILE5a projects such emissions, these projections are based on the extrapolation of empirically derived correlations well beyond the range of the original data. In the complex model and all of its RFG related analyses, EPA also assumes that evaporative emissions are zero in the winter. EPA also ignores refueling emissions in the winter. However, valid winter refueling emission data do exist and were used to develop the MOBILE5a correlations. Also, refueling emissions occur primarily through the simple displacement of fuel tank vapors with liquid fuel. Due to higher winter RVP, gasoline has a significant vapor pressure even in cold winter temperatures. Other non-exhaust VOC emissions involve the adsorption and desorption of vapors in charcoal canisters. These phenomena are much more complex and not fully understood under winter conditions. They also tend not to be a priority for study, since the primary focus of VOC control is ozone, which is almost exclusively a summer problem.

## MTBE Fraction of VOC Emissions

The next step is to estimate the MTBE fraction of the VOC emissions presented above. Beginning with exhaust VOC emissions, Automotive Testing Laboratories (ATL), under contract with EPA, tested 30 vehicles over the Federal Test Procedure using 10 different fuels. One fuel (Fuel "C") contained 11 vol% MTBE and its other fuel parameters were designed to represent typical Phase 1 (i.e., 1995-1999) RFG. ATL found that MTBE represented 3.2% of total exhaust hydrocarbon (THC) emissions (14). For gasoline fueled vehicles, VOC emissions are essentially THC emissions with the exclusion of methane and ethane. Since methane and ethane together represented 16.4% of THC emissions, MTBE represented 3.8% of exhaust VOC emissions.

Oxyfuel must contain 2.7 wt% oxygen, as opposed to RFG's 2.0 wt%. Thus, when MTBE is used oxyfuel will contain 15 vol% MTBE instead of RFG's 11 vol%. The MTBE fraction of exhaust VOC should be proportional to the amount of MTBE in the fuel in this range of MTBE concentrations. Thus, based on the EPA data, MTBE should represent 5.2% of VOC exhaust emissions from oxyfuel.

The Auto-Oil program also measured speciated VOC emissions from 20 vehicles using a wide variety of fuels (15,16). A number of these fuels contained 15 vol% MTBE. The fuels tested were designed to maximize the differences in various controlled parameters (e.g., 0-15 vol% MTBE, 20-45 vol% aromatics, etc.). Thus, none of the fuels fully represents Phase 1 RFG. Also, the vehicles tested by Auto-Oil all had very low emissions, while those tested by ATL included both low and high emitters.

The MTBE fraction of exhaust total organic gas (TOG) emissions, which is very similar to THC, for the five MTBE fuels examined in the Phase 1 Auto-Oil urban airshed modeling study ranged from 2.2-3.8%, with an average of 2.6%, which is slightly lower than the 3.2% found by EPA (17,18). Only one fuel produced an MTBE fraction above the average, and this was the highest emitting MTBE fuel in the Auto-Oil test program (both aromatics and T90 were at the high end of the evaluated ranges). The other fuels all showed MTBE fractions in a very tight range (2.2-2.5%). Thus, there appears to be evidence that the MTBE fraction could be a function of TOG/THC emissions, with the fractions of MTBE increasing slightly as TOG/THC emissions increase. This could explain both the variation in the Auto-Oil data and the difference between the ATL and Auto-Oil results. As the ATL data was obtained on the more representative sample of vehicles and fuels, it was chosen for use here.

The general finding that the MTBE fraction of THC/TOG emissions is less than the MTBE fraction of the fuel is not surprising. Combustion creates a vast number of species of VOC. For example, one, two, and three carbon species can represent 20% of exhaust THC emissions and none is found in the fuel. Thus, fuel components tend to be under-represented in the exhaust relative to the fuel. Being an oxygenate and also the product of a reversible reaction between methanol and isobutylene, MTBE tends to decompose and burn relatively quickly upon ignition and would be expected to be represent well below 11% of exhaust VOC emissions.

The measurement of the MTBE fraction of non-exhaust emissions is more complicated than that for exhaust emissions, as the nature of non-exhaust emissions can change dramatically depending on the total amount of non-exhaust VOC emissions. Also, the historic FTP for evaporative emissions (first used with the 1978 model year and only just recently updated) was a fairly lenient test. Vehicles with properly functioning control systems produced very low emissions over this FTP.

Evaporative emissions arise from a variety of sources. Fuel is almost always permeating through non-metallic hoses or seeping through fittings and connections. These emissions are commonly called *resting losses*. Vapors also escape from the fuel tank whenever the tank is heated, as occurs when a vehicle is sitting during the morning and early afternoon (*diurnal emissions*) and when it is being used (*running losses*). Finally, when a car is parked immediately after a trip, fuel in the carburetor bowl (if the vehicle is so equipped) can evaporate and vapors can be released from the tank via a set of complex phenomena, including some heating from exhaust system components and previously built-up pressure. When the amount of tank vapors generated is low, the onboard charcoal canister can capture and store all the vapors for release during engine operation. In this case, total emissions are low and dominated by resting losses, which tend to reflect fuel composition. When tank vapor generation is high, the capacity of the charcoal canister can be exceeded and large amounts of vapor are emitted. The composition of these emissions reflect the lighter fuel components that exist in the tank vapor space. Thus, care must be taken to match measured VOC speciations to the types of emissions which were actually occurring during the test (19). If measured VOC emissions were low, the measured VOC speciations must only be used to represent permeation and seepage losses. If measured VOC emissions were high, the measured VOC speciations must only be applied to vapor losses.

Both EPA and Auto-Oil have recognized this problem and taken steps to ensure that the VOC speciations used match the mass VOC emissions being modeled. As was the case with exhaust emissions, the vehicles tested by Auto-Oil for evaporative emissions also had very low emissions, much lower than the in-use evaporative emissions projected by MOBILE5a. It is likely that resting losses dominated the measured emissions, since the heavier fuel components were heavily represented in the emissions. The initial urban airshed modeling sponsored by Auto-Oil used the measured VOC speciation for non-exhaust emissions (20). However, when Auto-Oil later evaluated the impact of olefins on ozone reactivity, they did not use the measured VOC speciation, but estimated the speciation of evaporative emissions through the use of a vapor generation model (21).

EPA examined measured speciations of evaporative emissions from a number of test programs in 1993 (19). EPA segregated the data based on the total amount of VOC emitted during the test. Low emission levels were labeled "pass" as these emissions were consistent with the in-use MOBILE5a emission levels during most ambient conditions from properly operating vehicles which would "pass" EPA's pressure and purge I/M tests. The higher emission tests were labeled "fail", since these would be indicative of emissions from vehicles with improperly operating control systems which would be likely to "fail" the pressure and purge I/M tests.

EPA estimated the MTBE fraction of VOC emissions for hot soak, diurnal and running loss emissions for both "pass" and "fail" situations (19). These estimates are shown below in Table 8

	VOC Emissions		VOC Fraction: Failed Vehicles	MTBE Fraction		
	g/mi	Fraction		"Fail"	"Pass"	Overall
Evaporative	0.273	0.483	0.722	0.125	0.052	0.105
Hot Soak	0.185	0.328		0.114	0.039	
Diurnal	0.088	0.155		0.149	0.078	
Running Loss	0.222	0.393	0.834	0.185	0.119	0.174
Resting Loss	0.07	0.124	0	—	0.079	0.079
Total VOC	0.565					0.129

Also shown in Table 8 are a breakdown of non-exhaust emissions into their various sources, as well as the fraction of these emissions coming from "pass" and "fail" vehicles or situations. (Refueling emissions are not shown, as the pass/fail distinction does not apply.) The breakdown of non-exhaust emissions into evaporative (hot soak plus diurnal), running loss and resting loss emissions comes directly from the MOBILE5a modeling runs summarized in Table 3. The fraction of "pass" emissions was estimated by assuming that "pass" levels of diurnal, hot soak and running loss emissions were 0.5 grams, 0.4 grams, and 0.05 g/mi, respectively. Hot soaks were assumed to occur 5 times per day and vehicles driven 28 miles/day (45.05 km/day). These emission levels are indicative of those measured in the Auto-Oil program and other programs testing well-maintained vehicles (22). The fraction of "fail" emissions is simply one minus the "pass" fraction. The "fail" fraction of evaporative emissions was determined by simply mass weighting the "fail" fractions for hot soak and diurnal emissions.

EPA did not estimate an MTBE fraction for resting losses. Given that the "pass" levels of the other emission types are predominantly resting losses, the MTBE fraction of resting losses was estimated by averaging the "pass" MTBE fractions of the three other three emission categories.

Finally, the EPA estimates of the MTBE fraction of the various emission types were applied to the absolute mass emission estimates. These MTBE emissions were then summed and an overall MTBE fraction determined, which was 12.9%. This is a very reasonable estimate. The vapor pressure of MTBE tends to be very near that of gasoline, so the molar concentration of MTBE in fuel tank vapor should be near its fuel concentration, or 11 vol%. Since MTBE's molecular weight should be slightly higher than that of the average vapor component, a slightly higher mass fraction is not surprising.

Table 9 summarizes the MTBE fractions of the various emission types for the three fuels being evaluated. The MTBE fraction of refueling emissions was estimated to be the same as the "fail" fraction for diurnal emissions, since diurnal emissions in this situation best represent tank vapors under ambient conditions.



Table 9				
MTBE Fraction of VOC Emissions				
	RFG		RFG/Oxyfuel	Oxyfuel
	Summer	Winter	Winter	Winter
Exhaust	0.038	0.038	0.052	0.052
Evaporative	0.129	—	—	—
Refueling	0.149	0.149	0.201	0.201

#### Mass MTBE Emissions

This third step in the process simply involves multiplying the mass VOC emissions occurring when using oxyfuel and RFG by the MTBE fractions of VOC to produce absolute estimates of MTBE emissions. These are shown in Table 10 below.

Table 10				
MTBE Emissions				
Calendar Year/ Emission Type	RFG		RFG/Oxyfuel	Oxyfuel
	Summer	Winter	Winter	Winter
1995				
Exhaust	0.061	0.091	0.115	0.115
Evaporative	0.073	—	—	—
Refueling	0.007	0.007	0.01	0.01
Total	0.141	0.098	0.125	0.125
2000				
Exhaust	0.045	0.066	0.083	0.083
Evaporative	0.036	—	—	—
Refueling	0.005	0.006	0.008	0.008
Total	0.086	0.072	0.091	0.091
2005				
Exhaust	0.039	0.057	0.071	0.071
Evaporative	0.023	—	—	—
Refueling	0.003	0.004	0.006	0.006
Total	0.066	0.061	0.076	0.076
2010				
Exhaust	0.037	0.053	0.066	0.066
Evaporative	0.017	—	—	—
Refueling	0.003	0.003	0.005	0.005
Total	0.056	0.056	0.071	0.071

These estimates of the emissions of MTBE per mile can be converted to national emissions of MTBE in terms of tons per year by multiplying the emission factors by their respective fractions of national fuel consumption (or vehicle miles traveled (VMT), which is proportional to fuel consumption) and annual national VMT. The market shares of both RFG and oxyfuel in the U.S. were already discussed above. RFG alone represents about 25.8% of annual U.S. gasoline sales (or national VMT), while RFG/oxyfuel and oxyfuel alone represent another 9.4% and 3.0%, respectively. MTBE is the oxygenate used in roughly 80% of RFG and RFG/oxyfuel and is used in roughly 50% of non-RFG oxyfuel.

Total national VMT was projected from two EPA studies. The final EPA analysis supporting the RFG rule estimated 1998 VMT to be 2,343 billion miles per year (3,769.9 billion km/year). The EPA toxics study presented VMT growth factors for 1990, 1995, 2000, and 2010. These factors were converted to a basis of 1.0 for 1995 and used along with the 1998 projection to develop the VMT projections contained in Table 11. The growth factors for 1998 and 2005 were determined by assuming linear growth between 1995 and 2000 and between 2000 and 2010, respectively.

Year	VMT	% Change from 1995
1995	2230	0.00%
1998	2343	5.08%
2000	2418	8.46%
2005	2611	17.10%
2010	2803	25.73%

Conversion: 1.0 mile = 1.609 km

The above VMT projections and market shares for the various fuels were combined with the emission factors in Table 10 to produce the national MTBE emission estimates shown in Table 12. As mentioned above, the figures for oxyfuel include emissions from fuels meeting only the oxyfuel requirement and both the RFG and oxyfuel requirements. The figures for winter RFG represent emissions from fuels meeting only the RFG requirements.

Table 12

Total U.S. MTBE Emissions from Motor Vehicles (Tons/Year)

Year	Summer RFG	Winter RFG	RFG/Oxyfuel	Oxyfuel	Total
1995	55.720	23.316	28.828	9.200	88.237
2000	35.795	18.037	22.173	7.077	60.909
2005	28.182	15.638	19.156	6.114	49.933
2010	26.213	15.608	19.149	6.111	47.933

Conversion: 1 ton = 1,016 kg

As can be seen, MTBE emissions decrease after 1995 despite increasing VMT. This occurs because the in-use vehicle fleet is continuing to turnover to newer vehicles which meet the more stringent Tier 1 exhaust and enhanced evaporative emission standards which are being phased in with the 1994-98 model years. The effect of these standards can be seen from the VOC emission factors shown in Table 10. Between 1995 and 2010, exhaust VOC emission factors decrease by a factor of 1.5. Even more importantly, non-exhaust VOC emission factors decrease by more than a factor of 5. These reductions in g/mi VOC emissions more than counteracts the increase in VMT. While not directly used in the estimation of ambient MTBE concentrations below, the total tonnage of MTBE emissions may be of general interest to those interested in comparing total emissions of MTBE to the total emissions of other pollutants.

## AMBIENT CONCENTRATIONS OF MTBE (RAR)

Ambient concentrations of any motor vehicle pollutant can vary dramatically depending on both the level of emission and on the climatic conditions occurring at the time. The concentration of motor vehicle use, and therefore emissions, varies across an urban area and between rural and urban areas. As precipitation occurs over wide areas, an indication of MTBE concentration over a broad area is desired here, as opposed to peak concentrations at refueling stations or congested intersections.

EPA developed a Hazardous Air Pollutant Exposure Model specifically focussing on mobile source emissions (the HAPEM-MS model) (5). The model is based on both emission and ambient concentration measurements of carbon monoxide (CO), a pollutant coming primarily from motor vehicles. The theory behind the model is that the exposure to a pollutant is proportional to the emissions of the pollutant. For example, if MTBE emissions were 10% of the base CO emissions in the model, then the exposure to MTBE would be 10% that of CO. Emission factors for MTBE were developed in the previous section (Table 10). In this section, these emissions factors will be used in conjunction with HAPEM-MS to project ambient concentrations of MTBE.

There are two primary aspects to the model. The first addresses pollutant levels in various physical environments, while the second addresses the amount of time people spend in these environments. It is the first aspect that is most useful in this study.

One of the physical environments addressed by HAPEM-MS is the outdoors. HAPEM-MS's projected pollutant concentrations outdoors would be at ground level, which would likely be higher than those at higher elevations. Thus, HAPEM-MS's projections of MTBE in the atmosphere could be somewhat high for the purposes of this analysis and thus, overly conservative. However, the advantage of HAPEM-MS is that it considers the relative traffic density of both mid-size and large urban areas, as well as addressing rural areas separately. Also, the ambient concentrations were measured over longer periods of time relative to urban airshed models, which are typically run for only 1-3 days of simulation and focus on episodes having low dispersion characteristics.

The HAPEM-MS model projects that the average personal exposure to motor-vehicle related CO was 842 and 470  $\mu\text{g}/\text{m}^3$  in 1988 in urban and rural areas, respectively (5). However, this is based on an overall microenvironment exposure factor of 0.622, while the exposure factor for the outdoors (not immediately near a roadway) is 0.758. Thus, general outdoor CO levels would be higher by the ratio 0.758/0.622. While EPA developed its estimate of CO emissions using MOBILE4.1, it indicated that MOBILE4.1 underestimates CO emissions by 30-35% relative to MOBILE5a. Because the above MTBE emissions are based on MOBILE5a, the base CO emissions leading to the measured ambient CO exposures should also be based on MOBILE5a. Running MOBILE5a under the same summer and winter conditions as used to develop the VOC emission factors in Table 3 yielded an annual average 1988 CO emission factor of 42.45 g/mi. Finally, vehicle travel has increased since 1988. Per EPA estimates, emissions (and thus, ambient concentrations) should be increased by a factor of 1.123 for 1995. Taken together, these factors imply a ratio of ambient pollutant concentration to emission factor of 27.15 and 15.15  $\mu\text{g}/\text{m}^3$  per g/mi in urban and rural areas, respectively. Estimates of VMT growth for post-1995 years were taken from Table 11. Applying these factors to the emission estimates developed in the previous section produces the following average, ambient MTBE concentrations (Table 13).

Table 13				
Ambient MTBE Concentrations: HAPEM-MS Model: Outdoor ( $\mu\text{g}/\text{m}^3$ )				
Calendar Year	RFG		Oxyfuel/RFG	Oxyfuel
	Summer	Winter	Winter	Winter
Urban				
1995	3.81	2.66	3.39	3.39
2000	2.53	2.13	2.69	2.69
2005	2.08	1.93	2.43	2.43
2010	1.93	1.92	2.42	2.42
Rural				
1995	2.13	1.49	1.89	1.89
2000	1.41	1.19	1.5	1.5
2005	1.16	1.08	1.36	1.36
2010	1.08	1.07	1.35	1.35
HAPEM-MS Model: Outdoor (ppbv)				
Urban				
1995	1.26	0.88	1.12	1.12
2000	0.83	0.7	0.89	0.89
2005	0.69	0.64	0.8	0.8
2010	0.64	0.63	0.8	0.8
Rural				
1995	0.7	0.49	0.62	0.62
2000	0.47	0.39	0.49	0.49
2005	0.38	0.35	0.45	0.45
2010	0.35	0.35	0.44	0.44

As mentioned above, the HAPEM-MS exposure projections are based on CO emissions and measured ambient concentrations. CO is a relatively inert compound. Under high ozone conditions, its relative reaction rate is nearly two orders of magnitude smaller than that of MTBE.<sup>6</sup> The same relative comparison would be expected to be true at lower temperatures, as well. In its air toxics study, EPA estimated that the residence time of benzene in the atmosphere is roughly 60-110 hours in the summer and 37-120 days in the winter (5). MTBE is roughly 1.5 times as reactive as benzene, based on its Carter MIR (maximum incremental reactivity) factor of 0.62 gram ozone per gram organic versus 0.42 for benzene. Using a residence time of 85 hours for benzene, MTBE's residence time should be roughly 58 hours in the summer and 25-80 days in the winter.

<sup>6</sup> CO has a Carter ozone maximum incremental reactivity (MIR) factor of 0.0054 gram ozone per gram CO, while MTBE's MIR factor is 0.62 gram ozone per gram MTBE.

Assuming the urban ambient CO levels projected by HAPEM-MS apply to Detroit, the half life of inert CO based solely on dilution with fresh air is 29.9 hours<sup>5</sup>. Thus, MTBE's residence time in the winter is long enough to not be a factor. However, in the summer, this is long enough for 30% of the MTBE to react and form other compounds. Also, a few days often pass without any appreciable precipitation. Thus, beyond the urban area, an even higher percentage of ambient MTBE is likely to be destroyed in the summer before it has a chance to be absorbed by precipitation. Assuming 3-5 days between rainfall, 58-76% of the MTBE emitted would react prior to being absorbed. Again, in the winter, atmospheric reaction is unlikely to significantly decrease ambient MTBE levels.

A comparison of the concentrations projected in Table 13 with the small amount of ambient MTBE sampling data which exist generally confirms the above projections. One recent study measured MTBE levels around Milwaukee during January and February 1995, after the start of the RFG program there. Very limited fuel sampling indicated that MTBE was the oxygenate used in roughly half of the fuel. The average of eight 24-hour average samples around the University of Wisconsin at Milwaukee found MTBE at 0.2-0.3 ppbv. Nine measurements near roadways indicated a wide variety of MTBE levels, ranging from 0-1.5 ppbv, with only one site showing a level above 1.0 ppbv. Given the fact that MTBE was used in roughly 50% of the RFG and Milwaukee is not an oxyfuel area, the above methodology would project an ambient MTBE level of 0.44 ppbv. As this level is 50-100% higher than the University of Wisconsin readings and very close to the average measurement near roadways (which HAPEM-MS predicts should be a third higher than outdoor levels away from roadways), this indicates that the HAPEM-MS projections may overestimate the actual ambient level. However, any conclusions drawn from such limited data should be used with caution. Also, the Wisconsin measurements were taken near ground level. MTBE levels at higher altitudes should be much less, arguing further that the HAPEM-MS projections are worst-case in nature.

The fact that MTBE degrades in the atmosphere under both winter and summer conditions also means that the concentration of MTBE will not build up in the upper atmosphere. During the summer, MTBE's short residence time means that the majority of MTBE has already reacted by the time the air of the urban plume has had a chance to mix with air further downwind and air at higher altitudes. During the winter, MTBE's longer residence time provides more of a chance for mixing at higher altitudes. However, 80 days is still far too short for appreciable accumulation to occur given dilution will continue for even longer periods. The only way for accumulation to occur would be for the total volume of air in the atmosphere to be less than 80 times that of the breathing zone over areas where MTBE were emitted. The ambient CO levels used to develop the HAPEM projections only represent pollutant concentrations within 100 feet (30.48 meters) of the ground. Even if they represented MTBE concentrations in the initial 1000 feet (304.8 meters) of the atmosphere and were used throughout the world to the extent it is currently used in the U.S., MTBE would be diluted far more than a factor 80 times relative to its concentration in the urban breathing zone. Thus, there is no possibility of any appreciable build-up in the atmosphere.

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<sup>5</sup> Surface area = 6,566 square miles (16,998 square km); 1990 population = 5,187,000; VMT of 49.45 billion miles (79.57 billion km); mixing height of 1,640 feet (500 m).

## MTBE'S DISTRIBUTION IN THE ENVIRONMENT (WJP & DJB)

The following sections examine MTBE's potential to move and disappear in the other environmental mediums. Considered first will be the equilibrium concentrations in the other mediums to determine the driving force for MTBE to transfer there. Second, the transfer pathways will be discussed. Third, the potential for disappearance or accumulation in the various compartments is reviewed.

### MTBE's Equilibrium Among Environmental Phases

Relative to most gasoline VOCs, MTBE has a higher water solubility and a lower Henry's Law coefficient. This gives MTBE an equilibrium that is more favorable to the water phase. The distribution of MTBE between air and water phases is shown as a function of the mass ratio of air to water and the temperature in Figure 2. Under almost all conditions in the environment where MTBE will be found, the MTBE in water would be expected to contain less than 50 percent of the MTBE. For most of these conditions, less than 10% of the MTBE will be found in the water system. However, this equilibrium distribution is still greater than the initial distribution of MTBE releases of less than 1% into water supplies and soil as shown in Figure 1. Therefore, an equilibrium driving force seems to exist for MTBE to transfer from the atmosphere to the water supplies.

A simple equilibrium model outlined by Neely and Mackay (11) can be used to establish the potential equilibrium concentration for MTBE in water, soil and biomass (fish) as a function of the MTBE concentration in air. Using the information from Table 2B, the equilibrium concentrations at 25 °C are shown in Figure 3A. In an earlier section, the maximum MTBE concentration for summertime reformulated gasoline areas was estimated at a little less than 2 ppbv in the atmosphere. Therefore, based on Figure 3A summertime rain should have no more than 0.4 µg/L of MTBE dissolved into it if equilibrium can be achieved. If the water supplies were also to reach this equilibrium, the MTBE content in fish should be no higher than 0.6 µg/L while the MTBE content in soil would be less than 0.1 µg/L.

Lower temperatures reduce MTBE's volatility and Henry's Law Coefficient and increases its solubility in water. This leads to potentially higher equilibrium concentrations in water (and other mediums). The possible impact of colder temperatures is shown in Figure 3B which increases the MTBE equilibrium in freezing rain to a little over 2 µg/L and equilibrium content in soil up to 0.5 µg/L. These levels can only occur if the MTBE in the atmosphere achieves the maximum 2 ppbv, and then only if the transfer rates permit the equilibrium to be achieved and no degradation mechanism develops in the water phase. The evidence to date suggest that MTBE background levels are less than the 2 ppbv in the general atmosphere.

The simple compartment world model outlined by Neely and Mackay (11) assumed the surface area of water was 70% relative to the land mass for their mass distribution analysis in the model compartments (environmental phases). This provided an air / water mass ratio in the model compartments that is approximately equal to one. However, because of its limited atmospheric life (discussed later), MTBE's sphere of distribution will probably be limited to the area over land masses which only average a 4 percent water surface area. This would move the air to water ratio closer to 10 or higher. Referring to Figure 2, the mass distribution of MTBE in the water should be less than 10 percent. Under moderately higher temperatures, the MTBE in the water will be less

Figure 2

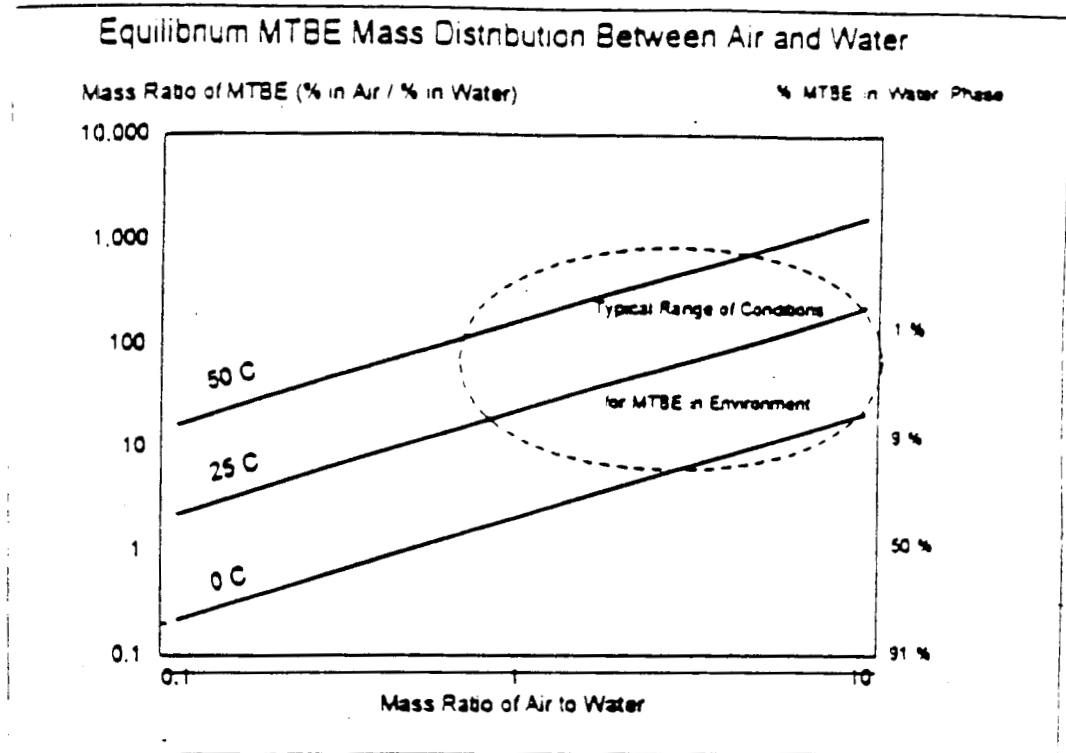




Figure 3A

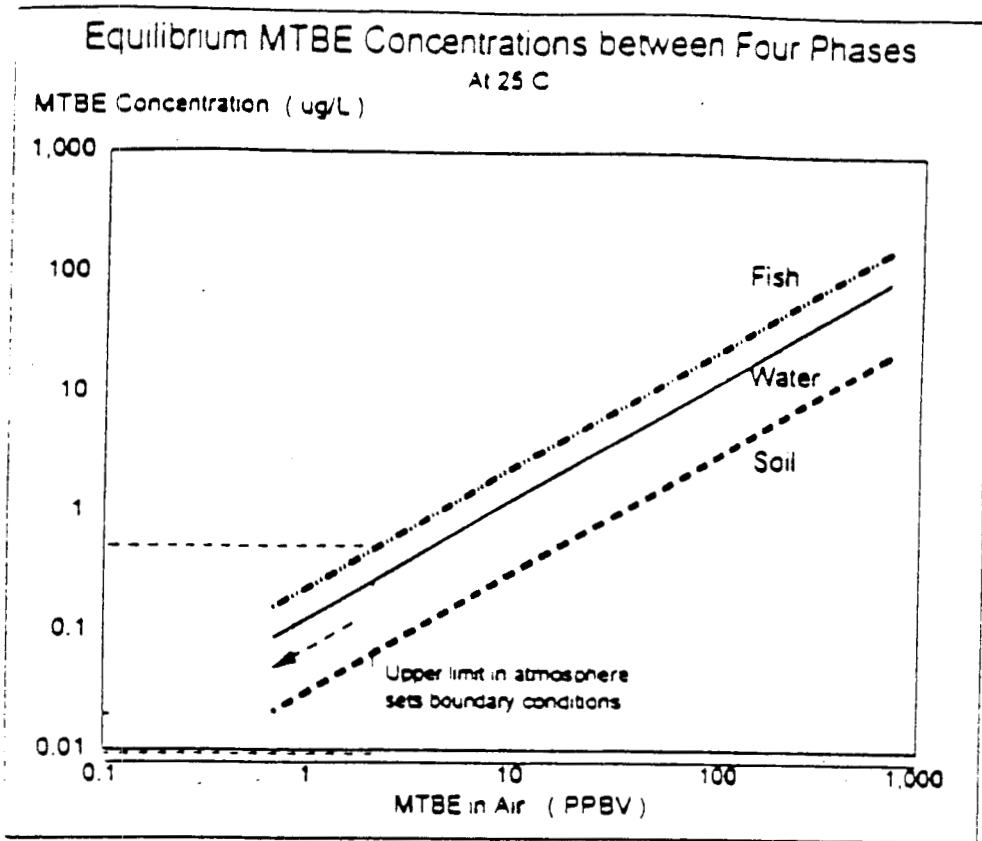
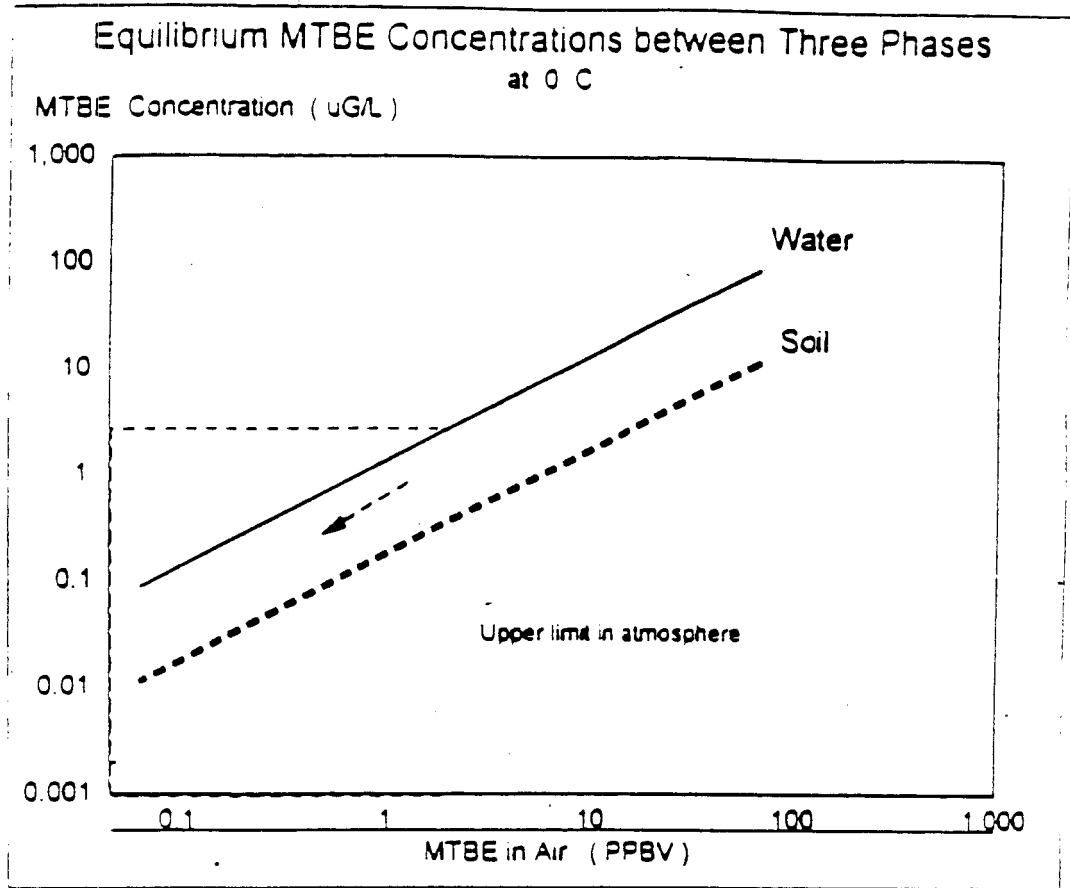


Figure 38



than 1 percent. The sensitivity to temperature suggest that the concentration and the mass of MTBE in the water may cycle with the change of seasons. However, the water supplies that have slow turnover (such as ground water and deep surface water bodies) should tend to dampen the concentration swings in the water.

## TRANSFER PATHWAYS FOR MTBE (WJP & DJB)

The equilibrium concentration of MTBE in the soil and biomass is mostly a function of the water concentration. Therefore, the controlling transfer rate is probably that between air and water. From the prior discussion, the equilibrium favors a transfer of MTBE from the air to the water. For VOCs, the main transfer mechanism from air to water is generally wet deposition (i.e. rain, ice or snow) and dry deposition (particles). Dry deposition usually only becomes a significant factor in the transfer for SVOCs (semi-volatile organic compounds) which have vapor pressures less than  $1 \times 10^{-4}$  mm Hg (23, 24). However, an EPA analysis does suggest that dry deposition may be playing a minor role during the summer for benzene (25). With MTBE's higher volatility, only wet deposition is expected to be major transfer mechanism for MTBE from air to water.

The MTBE occurs in wet deposition (i.e. wet precipitation) by being dissolved into the precipitation water. Equilibrium concentrations and mass transfer processes dictate that MTBE does not occur in wet precipitation as a pure (neat) solvent.

The limiting factor on the transfer of a VOC from air to the wet deposition carrier (rain) is the equilibrium concentrations determined by the Henry's Law coefficient. From earlier discussions, the maximum concentration for MTBE in cold weather rain is approximately  $2 \mu\text{g/L}$  when using the maximum air concentration of 2 ppbv. During warm weather, the maximum concentration in rain should be probably  $0.4 \mu\text{g/L}$ . A simple annual mean (i.e. not a temperature weighted average) would be  $1.2 \mu\text{g/L}$  of MTBE dissolved into wet deposition.

To estimate the potential transfer of MTBE from the atmosphere to the water surface, the estimated rainfall in the regions using gasolines containing MTBE needs to be determined. The annual rainfall in the U.S. is estimated at 4,000 billion gallons per day (15,140 trillion liters per day) (26). Based on the information from the U.S. Statistical Abstracts, the approximate continental U.S. landmass area is 3,732,400 square miles (9,666,900  $\text{km}^2$ ). This provides a U.S. average of approximately 24 inches (70 cm) of annual rainfall. The areas using the MTBE containing gasolines represent about 12 percent of the land surface. From the Statistical Abstracts, the average rainfall in this area is near 30 inches (76 cm). This provides a rain volume equal to 1,900,000 billion pounds ( $862 \times 10^{12}$  kg) per year that may precipitate through an atmosphere containing MTBE. Applying the  $1.2 \mu\text{g/L}$  concentration to all this wet precipitation gives a potential 2.3 million lbs. / yr (1 million kg/yr) of MTBE in the rain assuming a very conservative one hundred percent transfer efficiency. However, the percent of water that percolates to the ground water is only about 3.6 percent of the annual rainfall (26). Most of rainfall runs off into surface waters, and the rest usually evaporates or transpires back into the atmosphere. This provides a potential net transfer of only 82,000 lbs (37,000 kg) per year of MTBE into the ground-water system via wet precipitation.

Since the turnover of the deeper ground water is very slow, it could take hundreds of years for the average MTBE concentration in the deeper ground water to build-up and approach the concentration of that in the rainwater recharging these systems. However, many surface waters turnover much faster (usually less than a year), and therefore have the capability for their average concentration to approach that of the rainwater (annual mean of  $1.2 \mu\text{g/L}$ , maximum of  $2 \mu\text{g/L}$ ) in a relatively short period of time.

Like the aromatics, MTBE acts more volatile in water which helps it to quickly vaporize from open waters such as rivers and lakes when the air above it has little or no MTBE. The concentration half-life for turbulent surface waters such as rivers have been estimated for MTBE at about 9 hours (27, 28) relative to 5 hours for benzene (29). Therefore, the little MTBE that does

get into surface waters should quickly escape as the waters move away from urban air basins containing MTBE.

There is a general lack of analytical data regarding MTBE content in wet precipitation. MTBE has been measured in snow by the USGS in the Denver, Colorado area (30). This limited sampling (six samples) found MTBE in snowfall near Denver at a median concentration of 0.05 µg/L. These same snow samples also detected the presence of toluene (median = 0.05 µg/L) and benzene (median = 0.02 µg/L). Snow and ice have been identified as a potential deposition pathway for VOCs such as aromatics, but the process is still not fully quantified (31, 32). If these very low MTBE levels measured by the USGS are representative of the equilibrium concentrations for MTBE in snow, then the carrying capacity of this pathway should be very minor relative to that of rain.

The most effective process for transferring MTBE from gasoline to ground water is through the direct contact that may occur with blended gasoline spills or UST leaks. This issue is covered in much greater detail in subsequent sections of this paper.

#### MTBE Disappearance and Accumulation

Much the same as aromatics, MTBE can potentially disappear (degrade) from the various environmental compartments by a number of means. Like other VOCs, MTBE in the atmosphere oxidizes to intermediate products that eventually further oxidize to water and carbon dioxide. Other possible degradation sinks are biodegradation and hydrolysis in soil and water.

MTBE will readily oxidize in the atmosphere to a number of intermediate VOC products (33) shown in Table 14. As with other VOCs in the atmosphere, these higher oxygen products are expected to continue oxidizing to the ultimate products of carbon dioxide and water. The hydroxyl reaction rate for MTBE is measured as  $2.99 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup>sec<sup>-1</sup> at 298 °K. Based on this rate, the atmospheric life-time of MTBE under summer time conditions is estimated to be approximately 4 days. Under wintertime conditions, the atmospheric life-time will increase to 30-100 days depending on conditions. Atmospheric oxidation is expected to be the major route for MTBE disappearance from the environment.

Table 14		
Intermediate Product Yields From MTBE Atmospheric Oxidation		
	Moles / Mole of MTBE	Percent of MTBE Carbon
TBF (tertiary butyl formate)	0.68	68
Formaldehyde	0.48	9.6
TBA (tertiary butyl alcohol)	0.062	5.0
Methyl acetate	0.14	9.0
Acetone	0.026	1.6
Other	Unknown	6.8

MTBE has been shown to be biodegradable under waste water treatment conditions after the colony of organisms has been acclimated to MTBE in the waste water feed (34). A number of studies suggest that MTBE is not readily degradable by organisms naturally found in the environment (34, 35, 36). However, biodegradability in the soil or water is dependent on the prior contamination history (37, 38). Other studies (28, 34, 37, 39, 40, 41) show signs that MTBE will biodegrade slightly under both aerobic and anaerobic conditions. Fujiwara's study (28, 39) estimates the half-life for MTBE as between 28 and 180 days for aerobic biodegradation in surface waters and between 112 and 720 days for anaerobic biodegradation in deep water or ground water. These rates are much slower than those experienced for aromatics such as benzene. Based on these rates, biodegradation will not play a significant role for MTBE disappearance in surface waters since the half-life for volatilization is less than a day. However, depending on the available organisms, biodegradation may contribute to MTBE disappearance in some shallow ground-water systems since the water turnover is much slower (years to tens of years).

The potential for hydrolysis was also measured for MTBE. Hydrolysis does not appear to be a potential degradation process of any significance in surface waters since no measurable disappearance was detected (as per USEPA guidelines) in a 10 day period (3). This is considerably longer than the concentration half-life due to volatilization which appears to be less than a day.

One concern is that MTBE in wet precipitation may somehow be accumulating in the ground water to a much higher concentration than that in the recharge source (ex. rain). Other than by the bio-concentration process, there does not appear to be any other natural process for increasing the concentration of MTBE in the water supplies. As discussed earlier (Table 2A & 2B), the bio-concentration factor for fish appears to be very low which makes it difficult to bio-magnify MTBE in the food chain (Figure 3A). On the other hand, MTBE will readily volatilize from water at a rate faster than the water itself. Also, biodegradation does appear to occur in some cases. Both these processes will naturally work to decrease the concentration of MTBE in water supplies.

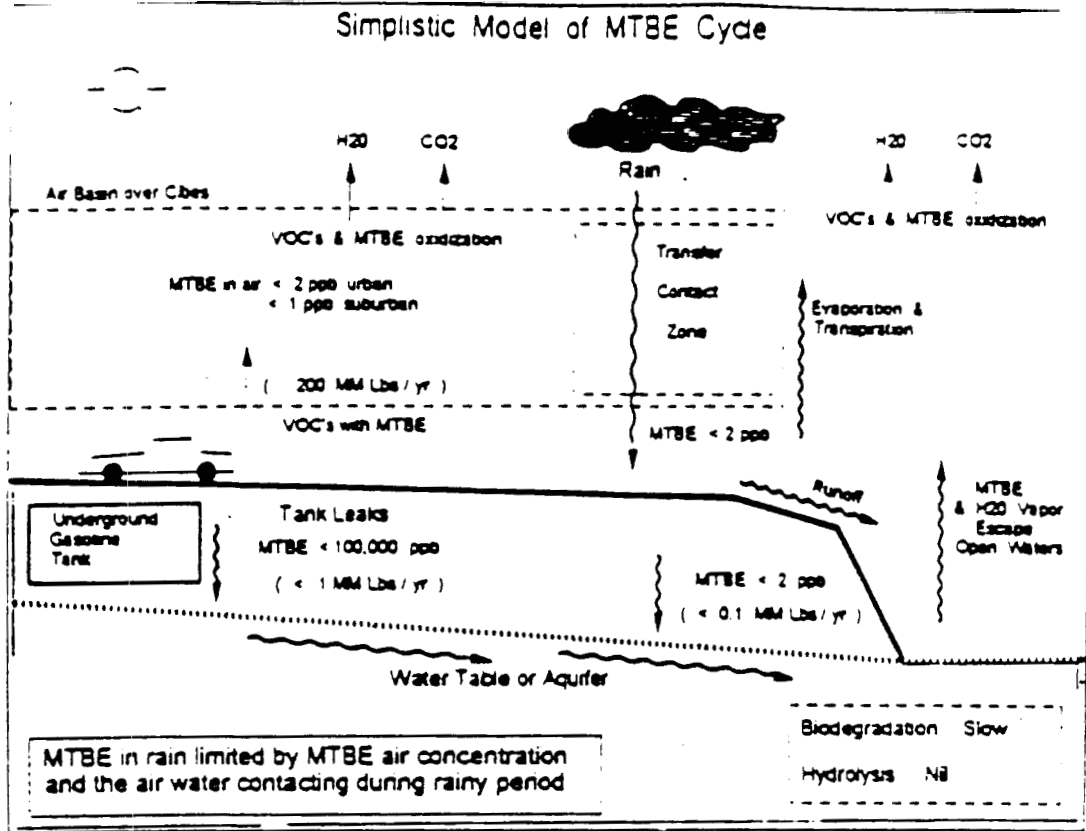
## MTBE Fate and Life-Cycle in the Environment

After reviewing the various degradation and transfer processes, a simple MTBE cycle can be developed to illustrate the expected movement of MTBE in the environment (Figure 4). This illustration does not include the minor sources of MTBE released by industry, but those releases essentially parallel the ones shown in Figure 4.

The mass balances and flows in the diagram show most of the MTBE releases going into the atmosphere over urban areas (gasoline consumption areas) where it disperses and degrades under natural oxidation processes. Because of its partial water solubility, some of the MTBE will move into the water supplies via wet precipitation or by gasoline leaks or spills. Some of this MTBE may biodegrade slowly, but most is expected to disperse as the ground water moves, and eventually volatilize back into the atmosphere from surface waters. Once back in the atmosphere, the MTBE is ultimately oxidized away. The MTBE concentrations along the transfer pathways in the cycle are expected to be low ( $< 2$  ppb) except for local ground-water regions near blended gasoline leaks. MTBE concentrations in these areas can be higher than  $100,000 \mu\text{g/L}$ , but are usually lower. These higher concentrations may be both unhealthful and an annoyance in drinking water because of MTBE's low odor thresholds. Therefore, in cases of high MTBE concentrations from gasoline leaks, the natural transport and degradation processes will likely be too slow to correct the problem and therefore some assistance may be required to remove the MTBE from the water supplies via known remediation methods.

The cycle described here is expected to be similar to the one that exists for benzene except that the expected flows and relative degradation rates will be different. Also, industry sources contribute a significant share of the benzene releases. However, the total amount of benzene released from gasoline sources is expected to decrease significantly because of the use of MTBE. The total amount of MTBE (and benzene) being released from gasoline into the atmosphere in the U.S. will also decrease substantially as VOC control regulations and UST regulations are fully implemented in the future. The surface water and the ground water portions of this life-cycle are analyzed in greater detail in subsequent sections of this report.

Figure 4





**PATHWAYS OF MTBE DISSOLVED INTO WET PRECIPITATION**  
(all subsequent sections written by JMD)

When wet precipitation falls from the atmosphere it can follow one of several paths (42):

- evaporate as it falls and return to the atmosphere
- reach the ground surface and then evaporate
- reach the ground and infiltrate (recharge) directly into the soil
- fall directly into surface water
- run across the ground surface as runoff which then reaches a surface water body or infiltrates into the soil

Any MTBE dissolved into the wet precipitation may follow the same pathways. As such, MTBE in wet precipitation may act as a non-point source of MTBE that might impact surface water and/or ground water. This is discussed below.

**Pathways to Surface Water**

Some wet precipitation falls directly into surface water bodies. Other wet precipitation may reach surface water via runoff. If it is present in wet precipitation, dissolved MTBE (at 2  $\mu\text{g/L}$  or less) may also directly, and immediately enter the surface water. However, the volume of water in most surface water bodies is far greater than the volume that recharges it in a single precipitation event. The large volume of water in the surface water body causes massive dilution, which means the incoming MTBE concentrations in the surface water must be substantially reduced. The deeper the surface water body, or the smaller the precipitation event, the greater the dilution. Regardless of rain storm intensity and the dimensions of the surface water body, concentrations in the surface water body must be diluted below the incoming maximum concentration of 2  $\mu\text{g/L}$  (see Example #1).

#### Example #1

Assume a one inch (2.54 cm) rainstorm event occurs (a one-inch rain storm is considered a large event).

Assume all the precipitation has the theoretical maximum MTBE concentration of 2.0  $\mu\text{g/L}$ .

Make very conservative assumption that no MTBE is lost to:

- volatilization as the precipitation fell
- volatilization from the surface water body

If the rain falls directly into a surface water body that is 8 feet, or 100 inches (254 cm) deep, then:  
=> the 100 inches of standing water will dilute the incoming precipitation at 100:1, thus resulting in a maximum MTBE concentration in ground water of 0.02  $\mu\text{g/L}$  (this is almost too low to quantify).

After this initial dilution takes place, MTBE volatilization from the surface water body will occur and reduce concentrations even further. Over the time frame of hours to days, volatilization is expected to continually, and efficiently remove MTBE from the surface water. Therefore, surface water concentrations should be far lower than 2  $\mu\text{g/L}$ , and may often be so low as to be not detectable.

Even addition of more MTBE-containing wet precipitation into surface water already affected by previous MTBE-impacted precipitation events could not cause concentrations to buildup. This is because mass transfer processes dictate that a contaminant's concentration in a receiving water (i.e. surface water) cannot exceed the concentrations in the original source water (i.e. wet precipitation) unless some accumulation mechanism exists. There is no known natural process by which MTBE concentrations can "build-up" or accumulate (physically, biologically, or chemically) in surface water to concentrations higher than the incoming sources.

In the early part of a rain event, surface runoff is zero as the wet precipitation evaporates back into the atmosphere and infiltrates into the soil. As a storm continues with time, some wet precipitation accumulates on the land surface as runoff (42). This runoff moves laterally downhill towards surface water bodies and so the runoff may reach a surface water body in a matter of minutes.

If MTBE is present in the wet precipitation that accumulates as runoff, then the runoff may carry some MTBE into the surface water body. Again, the MTBE concentration of the runoff must be equal to, or more likely, less than the wet precipitation. Therefore, even under unrealistically "worst-case" conditions, runoff of wet precipitation may sometimes be adding dissolved-phase MTBE into surface water bodies at concentrations less than 2  $\mu\text{g/L}$ . Once again, substantial dilution and volatilization should cause MTBE concentrations in the surface water body to be far less than 2  $\mu\text{g/L}$ , probably non-detectable.

### Interaction With Plants and Sediments

If MTBE-impacted runoff water encountered plants or sediments the chemical interaction should be minimal. MTBE has a very low Bio Concentration Factor (Table 2B).

Another important consideration is *adsorption* which is a bonding phenomena in which contaminants attach to solid particles. In the case of dissolved-phase contamination, adsorption can remove contaminants from the water and hold it onto a solid particle. Studies have shown that MTBE is poorly adsorbed by even pure organic carbon (43, 44). As such, MTBE should not be strongly attracted to the organic matter on the ground surface including plants, organic debris, and the soil itself (28). In addition, the exposure time to the runoff is quite small (minutes for most events) which even further limits the possibility of adsorption. This same poor adsorption tendency also limits MTBE's ability to adsorb onto sediments in a surface water body (45).

### Pathways to Ground Water and Soil

#### Definitions

*Ground water* can be defined as "subsurface water that occurs beneath the water table in soils and geologic formations that are fully saturated" (p. 2 of Reference 46). Although ground water can move vertically through soil or bedrock (collectively called *aquifer materials*) in the shallow subsurface, most movement is lateral. The ground water flows through open pores in between the grains of soil and/or through secondary fractures in the aquifer materials. As a result, ground-water movement is slow; in a typical sandy aquifer, ground water may move 10 - 1,000 feet (3 - 304 meters) per year, although the range can vary greatly.

When rain water infiltrates downward through the soil (due to gravity) some may remain in the soil pores (absorption), but some will reach the ground water. This process, known as *recharge*, adds water to the ground water. In addition to recharge from the infiltration of precipitation, ground water may also be recharged by leakage from surface water bodies. The opposite is also true in that ground water can "lose" water to a surface water body. Individual households and cities sometimes use ground water as their water supply by extracting it via water-supply wells.

#### MTBE Infiltration to Ground Water

Dissolved-phase MTBE (at 2 µg/L or less) may reach the ground water via infiltration of wet precipitation. When the infiltrating water moves slowly downward, a portion of the MTBE might volatilize into the soil gas and/or adsorb onto the soil matter. These processes act to reduce MTBE concentrations in the infiltrating water. In general, adsorption to organic soil matter slows the movement of an adsorbed component. Since the component attaches to the soil, on average it moves slower than the water. Because MTBE does not adsorb well, the rate of the MTBE infiltration will be essentially the same as the infiltrating water. Adsorption will be discussed further in subsequent sections of this report.

It is possible to sample infiltrating water from the vadose zone with lysimeters. Suction lysimeters seem to work best for monitoring dissolved VOCs (47) although the practice is not common. No references were found discussing MTBE measurements taken from lysimeter collected samples.

Appendix B contains calculations to determine the maximum MTBE concentration in ground water attributable to recharge by MTBE dissolved into wet precipitation. The calculations demonstrate how simple dilution by ground water prevents wet precipitation (even at the maximum modeled equilibrium concentration of 2 µg/L of MTBE) from ever creating ground water plumes of MTBE that exceed 2.0 µg/L. This is true no matter how many wet precipitation events with dissolved-phase MTBE occur (see Appendix B). These calculations used unrealistically conservative assumptions in order to model a "worst-case" scenario. Numerous real-world processes act to reduce MTBE concentrations even further including:

- volatilization of MTBE as the precipitation fell
- subsurface volatilization of MTBE into soil gas
- massive dilution by the ground water
- dispersion of ground water
- limited adsorption and/or biodegradation (possibly)

Therefore even if MTBE does occur in some wet precipitation, the ground-water concentrations it could create must be substantially below 2 µg/L, and quite probably close to zero. For example, in 1993-94, 562 shallow agricultural wells were sampled and analyzed by the United States Geological Survey (USGS). Many of these wells were in areas near, or downwind of, extensive MTBE use in gasoline. Only seven of the 562 ground-water samples (1.2%) had any detection of MTBE and the highest was 1.4 µg/L of MTBE (30, 48). This suggests that MTBE contamination of ground water by recharge of MTBE-impacted wet precipitation is not extensive.

#### MTBE Concentrations Cannot "Buildup" in Ground Water

Mass transfer processes dictate that a contaminant's concentration in a receiving water (i.e. ground water) cannot exceed the concentrations in the original source water (i.e. precipitation) unless some accumulation mechanism exists. As will be discussed later in this report, adsorption of MTBE is minimal to zero in soils. Therefore, the soils will not act as a "sink" of MTBE mass. Even if some adsorption occurred (perhaps due to high organic soils), there is no known "release" mechanism that would induce a high concentration of MTBE to suddenly released from the soil into the ground water. Therefore, adsorption to soil can not collect MTBE from infiltrating wet precipitation and later release it to cause MTBE concentrations greater than 2.0 µg/L in ground water. Due to MTBE's low Bio Concentration Factor, neither plants nor animals should act as any kind of MTBE sink or accumulation mechanism (45).

Therefore, there is no known mechanism (physical, chemical, or biological) that can cause MTBE dissolved into wet precipitation "build-up" or accumulate in the soil or ground water to concentrations greater than the maximum incoming level of 2.0 µg/L. As presented above, there are numerous processes that act to actually reduce MTBE concentrations in the ground water below the 2.0 µg/L theoretical maximum. Considering seasonal variations of temperature and MTBE concentrations in wet precipitation, the annual mean precipitation, and thus the maximum ground-water concentration, may be closer to 1.2 µg/L.

### Summary

Equilibrium concentration calculations predict that MTBE may occur in wet precipitation at concentrations of 2 µg/L or less. Therefore, MTBE in wet precipitation is a minor non-point source of MTBE in the ground water as its extent is quite limited (ex. only 1.2% of 562 shallow wells impacted) and its concentration is very limited (ex. 1.4 µg/L or less in the seven impacted wells).

### MTBE in Storm Water Runoff

Another possible non-point source of MTBE might be stormwater runoff that occurs during, and just after, larger precipitation events. As previously discussed, the precipitation that falls on the ground can only have 2 µg/L or less of MTBE. However in urban settings, as the runoff water crosses streets, parking lots, alleys and service station lots, it might encounter small spills of MTBE-blended gasoline and thus contain greater concentrations of MTBE.

Small spills of blended gasoline are expected in urban areas. Much of the spilled fuel (including MTBE) would be expected to volatilize quickly into the atmosphere, therefore the gasoline and MTBE potentially available on the ground surface is expected to be limited. Also, because it takes a significant rain event to initiate stormwater runoff, the large volume of precipitation water should greatly dilute any gasoline contaminant concentrations in the runoff. The mixing and movement of the water as it moves through culverts and ditches should promote volatilization of MTBE and aromatic hydrocarbons. Therefore, the concentrations of gasoline components in stormwater runoff should be quite small.

Runoff from parking lots and streets generally flows into ditches and culverts alongside the roads. These ditches are typically dry most of the time and then temporarily run with water during or immediately after a storm. While the metal culverts and concrete-lined ditches may initially prevent infiltration into the ground, most stormwater runoff routes eventually include a section of unlined ditch, discharge into an unlined retention pond, or discharge into a surface water body. Therefore, most stormwater has the opportunity to infiltrate into the ground and thus recharge ground water.

Stormwater samples were collected in four US cities that use MTBE-blended gasoline seasonally or all year (48). Of 279 samples collected, 39 samples (14%) had detections of MTBE. The concentrations ranged from 0.2 µg/L to 8.3 µg/L, and the median was 1.4 µg/L (48). Unfortunately, data regarding the presence of other aromatic gasoline components was not readily available from the USGS.

While MTBE is contained in some stormwater runoff, its measured concentrations are quite low. It is important to realize that the recharge of stormwater runoff occurs over only a very small portion of time (during and immediately after the storm), and over a very small area (only in the ditches, retention ponds, and areas immediately adjacent to paved areas). As such, MTBE in stormwater runoff can only produce ground-water concentrations substantially lower than those in the runoff due to:

- volatilization of MTBE during stormwater runoff transport
- limited amounts of MTBE-impacted recharging stormwater
- massive dilution by the ground water (see dilution mixing analysis in Example #1 and Appendix B)

Because of these factors, even the highest MTBE concentration noted in this study (8.3  $\mu\text{g/L}$ ) could only produce limited ground-water contamination of a few  $\mu\text{g/L}$ .

## SOURCES AND PATHWAYS OF MTBE IN GROUND WATER FROM BLENDED GASOLINE

### Pure MTBE

Pure (neat) MTBE spills could occur where the fuel additive is made or stored. Such spills might produce localized subsurface plumes of high MTBE concentrations (up to the pure compound solubility of 42,000,000  $\mu\text{g/L}$  at 20 °C). No pure MTBE spills to the subsurface have been encountered by the authors, or reported in the literature. Because only a few dozen industrial facilities make MTBE in the United States, such spills are quite rare, and not expected to cause public exposure to MTBE.

### Tank Bottom Waters from Aboveground Storage Tanks

Because MTBE is used in blended gasoline at up to 15% (volume/volume), the concentration of MTBE in gasoline can be 150,000,000  $\mu\text{g/L}$ . When dissolving neat (pure) MTBE into pure water, MTBE's maximum theoretical solubility is 42,000,000  $\mu\text{g/L}$  at 20 °C (Table 2B). However, when a blended gasoline is the source of the MTBE, the dissolved phase concentration can not reach this high. The MTBE will primarily stay in the fuel and some will dissolve into the adjacent water. The maximum concentration of MTBE in water from a blended gasoline is as follows:

$$C_{\text{max}} / K_{\text{ow}}^{\text{a}} = C_{\text{max}}$$

$$150,000,000 \mu\text{g/L} / 15.5 = 9,700,000 \mu\text{g/L}$$

Concentrations such as these will only be seen where very large volumes of fuel contact relatively small volumes of water (i.e. an "unlimited source" of MTBE), where contact time between the fluids is long, and where the water can not move away from the fuel before dissolving the maximum amount of MTBE possible. This typically only occurs to the "tank-bottom" waters inside above ground storage tanks of blended gasolines. Tank bottom water have been noted to have MTBE concentrations approaching 9,700,000  $\mu\text{g/L}$  (49). Historically, tank bottom waters were sometimes been discharged on to the ground surface although this practice is no longer common.

Therefore, a leak or discharge into the ground of tank bottom waters from an aboveground storage tank has the possibility of creating a local ground-water plume with MTBE concentrations as high as 9,700,000  $\mu\text{g/L}$ . Leakage or discharge of tank bottom waters with MTBE concentrations this high may have occurred, but certainly not all tank bottom waters were at the maximum possible concentration. Additionally, leakage or discharge of tank bottom waters is not a continuous flow, therefore the source would be limited. Therefore, a less than maximum concentration in seems likely for most tank bottom waters (49). Such leakage would also be greatly diluted by the ground water which would lower the concentration of any ground-water plume. Such a plume would only exist beneath, and immediately downgradient of, an aboveground storage tank facility where such a leak or discharge had occurred. The existence of a tankbottom

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<sup>a</sup>  $K_{\text{ow}}$  is the distribution coefficient between fuel and water.  $K_{\text{ow}} = 15.5$  as per Reference 50.

water caused MTBE plume has not been encountered by the authors, or reported in the literature. Therefore, it is believed that such plumes are rare, and are not expected to cause public exposure to MTBE.

#### Blended Gasoline

Gasoline is sometimes accidentally released into the subsurface through leaks, spills, or overfills at aboveground storage tanks, underground storage tanks, pipelines, or other petroleum handling facilities. The ubiquitous nature of petroleum fuels in modern society, combined with mechanical and human failures during production, transport and storage of the fuels causes gasoline releases to be fairly a common phenomena. These point source leaks usually produce localized ground-water contamination plumes.

If the spilled gasoline has no oxygenate additive, then typical ground-water contaminants include dissolved-phase benzene, toluene, ethylbenzene, xylenes, and many other aromatic and non-aromatic hydrocarbons. If the spilled gasoline has been blended with MTBE, then a dissolved-phase MTBE plume will also form. Approximately 30% of the gasoline currently sold in the United States contains the oxygenate additive MTBE and that percentage may increase as use of oxygenate additives increases (see Table 1). Therefore, some subsurface contamination by MTBE due to blended gasoline releases is expected.

#### Causes of Leaks

The most common cause of gasoline releases is failures of underground storage tank systems (USTs). For these USTs the major causes of leaks (S1) are:

- |                        |          |
|------------------------|----------|
| - tank leaks           | @ 43-58% |
| - piping leaks         | @ 20-35% |
| - overfill/spills      | @ 15%    |
| - loose fittings, etc. | ??       |

Many of these UST system failures are due to cracks (fiberglass), holes, rust, loose fittings, mis-measurements, and a variety of human errors. In addition to UST releases, gasoline can be released via similar mishaps at refineries, pipelines, tankfarms, and truck rollovers.



### MTBE Concentrations in Ground Water from Blended Gasoline Leaks

While the maximum theoretical concentration of MTBE in water from a blended gasoline source is roughly 9,700,000  $\mu\text{g/L}$ , in almost all cases MTBE concentrations in ground water reach anywhere near this level. This is because with subsurface blended gasoline spills

- the spill, and thus the MTBE supply, is limited in volume
- MTBE is often used in gasoline at less than 15%, which limits MTBE availability,
- MTBE's distribution coefficients for fuel/water mixtures ( $K_{ow}$  of 15.5) dictate that the MTBE would much rather stay in the fuel than in the water (50, 52),
- advective ground-water movement causes the water to move away from the spilled fuel before maximum MTBE solubilities can be reached, and
- the MTBE plume is diluted by the existing ground water
- MTBE concentrations are further reduced by 3-Dimensional dispersion as the impacted ground water moves downgradient

When investigating hydrocarbon spills, it is common to use EPA Method 8020<sup>7</sup> to quantify the BTEX and MTBE compounds. Table 15 summarizes the range of MTBE concentrations measured in the ground water near the source areas of numerous blended fuel leaks. These are sites where the MTBE was known to be due to blended gasoline releases. The MTBE concentrations can vary widely depending upon the individual spill circumstances, as well as where the sampled well was in relation to the spill. Typically, MTBE concentrations of 100 - 100,000  $\mu\text{g/L}$  are found near blended fuel spills, although values as high as 236,250  $\mu\text{g/L}$  have been reported in the literature (2).

A laboratory bench mixing experiment with water and blended gasoline showed that MTBE concentrations in water can reach 966,000  $\mu\text{g/L}$  (53). Another laboratory study found that MTBE from a blended gasoline saturated the water with MTBE when the MTBE concentration reached 336,000  $\mu\text{g/L}$  for a 92 octane gasoline (54). The ideal mixing situation used in these studies means these values likely represent the upper boundary for MTBE concentrations in subsurface ground water. Therefore, MTBE ground-water concentrations as high as 1,000,000  $\mu\text{g/L}$  may be possible under unusual subsurface conditions<sup>8</sup>, but at most spill sites the MTBE concentrations usually ranges from 100 to 100,000  $\mu\text{g/L}$ .

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<sup>7</sup> This is very similar to USEPA Method 802. Depending upon the laboratory, and several other variables, both these methods typically have a detection limit of 1  $\mu\text{g/L}$  to 5  $\mu\text{g/L}$  for MTBE.

<sup>8</sup> Care should be taken not to mix in results from MTBE water samples collected from tank bottom waters (49). The special storage circumstances and large volume of product exposed to tank bottom water can cause MTBE concentrations to reach 9,700,000  $\mu\text{g/L}$  (49), but values this high have never been reported for ground water.

TABLE 15

## MTBE OCCURRENCE IN GROUND WATER NEAR UST RELEASES

SOURCE	NUMBER OF WELLS	HIGHEST MTBE RECORDED (ug/L)	RANGE OF MTBE RECORDED (ug/L)	HIGHEST MTBE WITH NO BTEX PRESENT (ug/L)	REFERENCE
DAVIDSON	300	200,000	10 - 200,000	879	AUTHOR
GARRETT ET AL.	8	236,250	15- 236,250	690	2
MALLEY ET AL.	10	987	11- 987	NA	55
LUMRS & PYOTT	35	26,000	7 - 26,000	180	54

## Fuel Leak Trends

Prior to the mid-1980s, only a few state and local agencies had laws governing the operation and testing of USTs. As a result, leaking UST systems could release fuel undetected and unabated for extended periods of time. Repair and replacement of USTs were sometimes based on economics alone (i.e. cost of repairs vs. cost of lost fuel). In 1986 the USEPA estimated that approximately 20% of the 1,800,000 registered petroleum USTs were probably leaking and this estimate has held accurate (56).

On December 22, 1988 the UST regulations entitled "Technical Standards and Corrective Action Requirements for Owners and Operators of Underground Storage Tanks" became enforceable. These regulations established performance standards for new USTs and required leak detection, leak prevention, and corrective actions for leaks or spills (57). Reporting such leaks to appropriate agencies was also required. These federal laws were adapted by most states, and as a result:

- prevention measures are taken to avert and reduce leaks
- regular activities (tank gauging, tightness tests, etc.) are used to detect leaks sooner
- releases must be quickly reported and acted upon
- release impacts must be assessed
- where necessary, releases must be remediated

All these have combined to decrease the number of tanks in existence and to reduce the duration and sizes of leaks since the early 1980s. This has greatly reduced the amount of fuel released into the environment. As the final phases of the UST regulations become effective by December 1998, even more improvements should take place and reduce the total volume of fuel released even further.

These improvements can be seen by comparing mid-1980s release conditions against current information (tank populations, leak detection procedures, etc.) Based upon current trends, and the complete implementation of the UST regulations, estimates are made here regarding fuel release trends. Table 16 compiles these preliminary estimates.

**TABLE 16**  
**PETROLEUM UST RELEASE TRENDS**

<u>YEAR</u>	<u>PETROLEUM USTS IN SERVICE</u>	<u>EST. % STILL LEAKING</u>	<u>ESTIMATED MEAN LEAK DURATION (days)</u>	<u>TOTAL ESTIMATED LEAK-DAYS (days)</u>	<u>LEAK-DAY % DECLINE SINCE 1985</u>
1985	1,800,000 <sup>a</sup>	20 <sup>b</sup>	90 <sup>c</sup>	32,400,000 <sup>d</sup>	-
1995	1,000,000 <sup>a</sup>	10 <sup>b</sup>	56 <sup>e</sup>	5,600,000 <sup>d</sup>	83 <sup>f</sup>
2000	980,000 <sup>a</sup>	5 <sup>b</sup>	24 <sup>e</sup>	1,176,000 <sup>d</sup>	96 <sup>f</sup>

See Appendix C for an explanation of these superscripted notes (a through i), a discussion of the methods used, and a data quality review of Table 16.

Table 16 shows that number of petroleum USTs in service and the estimated percentage of tanks leaking have both declined from 1985 to 1995. Based on leak detection methods used and their frequency of implementation (i.e. monthly or annually), the average leak duration has been estimated to have declined significantly from 90 days in 1985 to 56 days in 1995. Over half the USTs are monitored monthly in 1995 (by one of various methods) as opposed to less than annual leak detection in the mid-1980s. This beneficial trend should continue as the UST program reaches full implementation after 1998 and most USTs come into compliance. It is estimated here that nationwide the number of leak-days has declined 83% since 1985 due to the UST laws being implemented and that by 2000, there will be a 96% decline in leak-days as compared to 1985.

**Mass of MTBE Lost From UST Releases**

As leak durations have decreased, the total volume of an individual leak must also have declined significantly. This decline in leak volume will be further augmented as the leak rate must have also declined due to the more sensitive test methods now being used, and to those methods being applied more frequently. As shown in Table 1, MTBE currently comprises approximately 3.5% of the nation's gasoline on a volume/volume basis. MTBE comprised approximately 0.05% of the nation's gasoline in 1985, and will comprise about 3.8% in the year 2000. Using these values, the number of leaking USTs, and the average tank leak volumes, estimates are made here regarding the volume of MTBE lost to the subsurface from USTs (Table 17). The volume of MTBE released to the subsurface via pipeline releases is not quantified here as no baseline values (leak rates, duration, monitoring data) for making such estimates were available.

**TABLE 17**

**MTBE VOLUMES LOST TO SUBSURFACE FROM PETROLEUM USTs**

<b>YEAR</b>	<b>PETROLEUM USTs IN SERVICE</b>	<b>EST. % STILL LEAKING</b>	<b># OF LEAKING USTs</b>	<b>AVERAGE GALLONS GASOLINE LOST</b>	<b>% OF GASOLINE THAT IS MTBE</b>	<b>EST. GALS. MTBE LOST</b>
1985	1,800,000 <sup>a</sup>	20 <sup>b</sup>	360,000 <sup>c</sup>	860 <sup>d</sup>	0.5 <sup>e</sup>	1,548,000 <sup>f</sup>
1995	1,000,000 <sup>a</sup>	10 <sup>b</sup>	100,000 <sup>c</sup>	400 <sup>h</sup>	3.5 <sup>i</sup>	1,400,000 <sup>j</sup>
2000	980,000 <sup>k</sup>	5 <sup>l</sup>	49,000 <sup>c</sup>	145 <sup>o</sup>	3.8 <sup>n</sup>	270,000 <sup>p</sup>

Conversion: 1 gallon = 3.785 liters

See Appendix D for an explanation of the superscripted notes (a through o), a discussion of the methods used and a data quality review of Table 17.

As shown in Table 17, there is nearly seven times more MTBE in gasoline in 1995 than in 1985. But in spite of this much more extensive use of MTBE, the amount of MTBE released into the subsurface from UST leaks has decreased slightly from 1985 to 1995. The decrease is due to:

- reduced UST population (measured)
- decreasing percentage of UST population leaking (measured)
- decreasing volume of gasoline lost per leak (estimated in this paper)

From 1995 to 2000, the amount of MTBE released into the subsurface from leaking USTs should decline even more as the 1998 UST regulations become fully applicable, as compliance improves, and as MTBE percentage in the nation's gasoline ceases to increase at the rapid rate seen from 1985 to 1995 (Table 1). The percent of MTBE in the nation's gasoline will stabilize at about 3.8 to 3.9% by the year 2000 as oxyfuel programs phase out. Therefore, even though MTBE use in gasoline is increasing, improvements in the UST population and regulatory compliance result in substantially less MTBE being released to the subsurface in the future.

## ANALYSIS OF MTBE MOVEMENT WITH GROUND WATER

Once a dissolved-phase contaminant is in the ground water, it will move adjectively with the ground water, and in the same direction. However, a solute's movement may be impacted by density flow, dispersion, adsorption, volatilization, biodegradation, or other mechanisms. The sections below will discuss to what degree each of these impact MTBE movement with ground water.

### Vertical Position of MTBE in Ground Water

In its pure state, MTBE has a dimensionless specific gravity of 0.735 (Table 2A) relative to pure water (1.00). As such, once dissolved into the ground water MTBE should not increase the ground water's density and so downward, density-driven flow is not an issue.

Whether MTBE reaches the subsurface via infiltrating precipitation, or by a local release of MTBE-blended gasoline, the introduction of MTBE is almost always in the shallowest portion of the shallowest aquifers. Therefore, MTBE will initially be found in ground water just below the water table surface. Shallow, lateral transport is maintained as horizontal hydraulic conductivity is typically ten times greater than vertical hydraulic conductivity for unconsolidated aquifers. Additionally, horizontal longitudinal dispersivity is also about ten times greater than vertical transverse dispersivity (58). This further promotes lateral movement of dissolved contaminants like MTBE, and discourages vertical movement. As a result of these two factors, shallow ground-water flow is primarily horizontal and the dissolved-phase MTBE tends to stay in the shallowest portion of the shallowest aquifers.

Field experience doing discrete ground-water sampling with depth has shown that aromatic hydrocarbons and MTBE compounds are almost always found in the first 10-20 feet (3 to 6 m) of the ground-water column beneath the water table, and only on rare occasions do they move deeper. Vertical concentration gradients are often steep as shown at one site where a well's greatest MTBE concentration was found between two and four feet (0.6 to 1.2 m) below the water table, while the deeper ground water had much lower concentrations (59).

A recent study sampled 211 shallow ground-water wells and springs in eight urban regions across the United States. In addition, ground-water samples were collected from 413 deeper ground water wells across nine regions of the country (48). In the shallow wells and springs, 27% of the 211 samples had MTBE detected while only 1.0% of the deeper wells had MTBE. In addition, of those four deeper ground-water samples with MTBE, the highest concentration was 1.3  $\mu\text{g/L}$  (48). While the depth of the deeper wells was not provided in the report, it is clear that these deeper wells are screened across the deeper, major water-supply aquifers. This study provides supporting evidence that MTBE contamination of ground water is generally limited to shallow portions of shallow ground-water systems.

## Dispersion of MTBE

*Dispersion* is the term applied to describe a series of micro-scale processes that act to spread ground-water contaminants in all three dimensions. As the plume moves downgradient, the same contaminant mass is dispersed over larger volume of ground water which reduces contaminant concentrations. Therefore, dispersion is an important mechanism for reducing concentrations, especially for a conservative contaminant like MTBE.

Dispersion in the direction of ground-water flow is longitudinal dispersion, while dispersion in the transverse and vertical directions perpendicular to ground-water flow are called horizontal transverse dispersion and vertical transverse dispersion, respectively. Field experiments often find longitudinal dispersivities to be two to six times greater than those estimated in the laboratory (58). This is because dispersion is complex property that seems to get larger as the scale of the plume increases. Empirically, longitudinal dispersivity has been seen to be equal to about one-tenth of the scale of interest (60).

Horizontal transverse dispersivity is often 0.05 to 0.2 that of longitudinal dispersivity (58) with a value of 0.1 used most often (61). Vertical transverse dispersivity is often assumed to be equal to horizontal transverse dispersivity (62) and so it too is about one-tenth of longitudinal dispersivity (58).

With greater horizontal transport distance and increased time, the cumulative effect of vertical transverse dispersion can cause some vertical spreading of a recalcitrant compound like MTBE. Some evidence of this may have been seen in field experiments where the MTBE appeared to go deeper into the aquifer as the transport time and distances increased (62). Computer modeling could be conducted to determine the impact that dispersion has in reducing dissolved-phase MTBE concentrations as the plume moves downgradient.

## Adsorption of MTBE

A component's tendency to adsorb to organic matter can be estimated by its organic carbon partition coefficient, or  $K_{oc}$ . As summarized in Table 2B of this report, the reported values of MTBE's  $K_{oc}$  range from 5.5 to 13.5, while other sources report values of 8.7 to 81.28 (45). These low values indicate that MTBE will adsorb poorly to organic matter. This is supported by ground-water remediation experience where granulated activated carbon (GAC) treatment systems are fairly inefficient at removing MTBE from impacted water long term (1, 44).

How well a solute attaches to soil depends upon the compound's  $K_{oc}$  and the soil's natural fraction of organic carbon, or  $F_{oc}$ . The controlling equation (46) is:

$$Rf = 1 - \frac{P_s \times (K_{oc} \times F_{oc})}{n}$$

where:

$Rf$  = retardation factor, or how much slower the solute moves relative to the ground water

$P_s$  = soil bulk density

$n$  = soil porosity

Due to the site-specific factors of soil porosity, soil bulk density and fraction of organic carbon in the soil, no universal retardation factor can be provided. However, using typical reference values (46, 61), a general estimate of MTBE retardation can be provided. Using:

porosity = 0.30 (i.e. 30%)

bulk density = 1.85 g/cm<sup>3</sup>

$F_{oc}$  = 0.0002 (i.e. 0.02%)

$K_{oc}$  = range of 8.7 to 81

Then a retardation value for MTBE ranges from 1.01 to 1.09. As a result of these very small retardation values, little to no MTBE usually attaches to the soil. This is supported by the vast collection of field experience from MTBE-containing gasoline spills which shows MTBE contamination of soil is an uncommon occurrence.

The vast majority of dissolved-phase MTBE that enters the subsurface will stay in the infiltrating water and then transfer to the ground water. A retardation value of close to 1.00 means the dissolved-phase MTBE moves at almost the same speed as the ground water. This compares favorably to a generalized contaminant transport modeling study reported by Piel (41) which determined an average retardation factor of 1.01 for MTBE and 1.09 for benzene.



In sandy units with low organic matter, the adsorption of MTBE would be nearly zero (i.e.  $R_f = 1.00$ ) while aromatic hydrocarbons would have retardation factors greater than 1.00. For example, the Borden aquifer in Canada is one such unit (61) and at this carefully studied site, the retardation factors were calculated as follows:

<u>CONTAMINANT</u>	<u>RETARDATION FACTOR RANGE</u>	<u>AVERAGE <math>R_f</math></u>
Chloride	1.00 - 1.00	1.00
MTBE	0.97 - 1.04	1.00
Benzene	1.05 - 1.19	1.14
Toluene	1.13 - 1.34	1.24
Ethylbenzene	1.37 - 2.34	1.86
p-Xylene	1.52 - 2.20	1.86
m-Xylene	1.34 - 1.46	1.40
o-Xylene	1.38 - 1.97	1.68

This field-scale study (61) showed that, as expected, in a sandy aquifer with low organic carbon content ( $F_{oc} = 0.021\%$ ) the MTBE moved at essentially the same rate as the ground water. Both the MTBE and a conservative (unretarded) chloride tracer had average retardation factors of approximately 1.00.

When comparing retardation factors for the aromatics in the presence of MTBE (10% in the gasoline) and in its absence (the control), this study found that the retardation factors for the aromatic components were the same (61). In other words, the presence of MTBE (10% in the gasoline) did not make the BTEX compounds move faster or further.

Because of its very limited to non-existent retardation, dissolved MTBE will move faster through the aquifer and thus be further downgradient than the BTEX compounds or other hydrocarbons (2, 61). A contaminant's retardation is directly dependent upon how much organic matter ( $F_{oc}$ ) is in the soil at each site and so standard retardation factors can not be provided. In general however, benzene will typically have a retardation factor of at least 1.1 in soils with low organic content, and it can be much higher for more organic rich soils. Since MTBE's retardation factor is usually close to 1.0, the MTBE will move at least 10% faster than the benzene in the same aquifer. Toluene, ethylbenzene, xylenes and other aromatic hydrocarbons typically have retardation factors of 1.1 to 2.0 (or more). Therefore, MTBE will migrate 20%, or more, faster than most aromatic hydrocarbons.

As the plume moves further downgradient, this faster migration of MTBE will remain constant in proportion (ex. 10% faster than benzene), but the absolute difference between the benzene front and MTBE front will increase. This is because as the total distance of plume migration gets larger, then 10% of that distance also becomes a larger value. For instance, consider a site where benzene  $R_f$  is 1.1 and the MTBE  $R_f$  is 1.00. If the dissolved-phase benzene plume has migrated 600 feet (183 m) away from the spill source, then the MTBE front would be expected to be approximately 660 feet (201.2 m) downgradient of the source due to retardation differences alone. As will be discussed below, differential biodegradation rates will cause the separation of the benzene front and the MTBE front to become even greater.

#### Volatilization of MTBE from Ground Water

It is well known that volatile contaminants can volatilize from the ground water and enter the subsurface air (soil gas) in the unsaturated soil pores above the water table. As such, volatilization could be an important process for removing MTBE from ground water. The Henry's Law Constant for MTBE at 25 °C has been determined to be 0.0216 (10). These values indicate that MTBE from water is about 1 order of magnitude less volatile than benzene (10).

A component's tendency to volatilize out of water can be quantified by the Henry's Law Constant. However, in order to estimate MTBE mass losses from the ground water due to volatilization, it is necessary to also consider vapor movement by diffusion. Diffusion determines the mass transfer rate of MTBE being carried away from the water/air interface in the soil. Then it must be determined how much MTBE mass is removed from the subsurface by transfer to the atmosphere and/or destroyed (by vapor phase biodegradation, etc.).

Subsurface volatilization of MTBE from the ground water might be especially significant after the MTBE plume has increased its size due to advective and dispersive ground-water movement. The same mass of MTBE spread over a larger portion of the aquifer means there is more surface contact between the MTBE ground-water plume and the unsaturated zone. This might allow more volatilization to take place. Additionally, as the MTBE migrates downgradient, it continually encounters regions where the subsurface air is not in equilibrium with the dissolved-phase MTBE. This helps perpetuate continuing volatilization of MTBE from the ground water.

However, these volatilization driving forces are eventually reduced. Since the MTBE concentrations in ground water are reduced as the plume grows through advection and dispersion, the vapor phase concentrations in the air above the contaminated ground water must also be reduced (i.e. Henry's Law). This means less MTBE will enter the vapor phase to be carried away, and so vapor phase removal of MTBE from ground water will be reduced.

Volatilization of MTBE and subsequent vapor-phase diffusion are certainly mass removal mechanisms that will reduce MTBE concentrations in ground water. Determining numerical values of volatilization-induced ground-water concentration declines would require multi-phase modeling that included:

- varying ground-water MTBE concentrations with space (range from 10 µg/L to 100,000 µg/L)
- volatilization rates from ground water (i.e. Henry's Law)
- diffusion of the vapor phase in subsurface soil that recognized reduced porosity in the soil due to water filled-pores and tortuous pores
- soil moisture and its impacts on porosity and diffusion rates
- MTBE mass loss due to atmospheric emissions
- MTBE mass loss due to vapor phase adsorption (if any)
- MTBE mass loss due to vapor phase biodegradation (if any)
- model capable of handling declining MTBE concentrations in ground water as the mass losses to the vapor phase occurred (i.e. varying MTBE concentrations with time).

Some realistic assumptions that would simplify the calculations might include

- no separate-phase MTBE exists in the soil or ground water
- MTBE concentration is zero in soil
- advective transport of vapors is zero
- vapor phase retardation is zero

Such a model was not performed in this report, but is a possible topic suggested for future study.

#### Vapor Migration

Since MTBE can volatilize from ground water and form a vapor phase, the possible fate and transport of those vapors must be considered. In addition to the gradual, multi-directional spread of vapors by diffusion, subsurface vapors also move advectively in response to total pressure gradients. Therefore, vapors will flow out into the atmosphere as the barometric pressure falls (63). This provides a mass removal mechanism for vapor-phase MTBE from the subsurface. Subsurface diffusion rates, a component's vapor pressure and vapor density can all change with temperature and so temperature variations also affect vapor phase transport (63).

Potential exposure to subsurface vapor-phase contaminants depends upon (64):

- contaminant concentration in ground water
- contaminant volatility in subsurface
- advective and diffusive movement of vapor-phase contaminants
- position of potential receptor (i.e. horizontal distance from contaminated ground water)
- thickness of unsaturated soil (i.e. vertical distance from contaminated ground water)
- attenuating factors that lower vapor concentrations (i.e. adsorption, biodegradation, etc.)

Buildings located directly over a ground-water contamination plume of volatile components represent a possible route of exposure to subsurface vapors. Vapor concentrations would probably be greatest in basements as the vapors likely enter through cracks in the basement walls or floor, and also air circulation is generally poorest in basements which can allow vapor accumulation. Buildings without basements or crawl spaces have a reduced likelihood of accumulating volatile vapors.

Volatile vapors would probably be greatest directly over separate-phase (pure) gasoline. High ground-water concentrations might also create a vapor-phase problem. Modeling that addresses vapor phase migration of MTBE towards building basements has not been conducted in this study, but may be a possible topic for future research.

If a specific scenario is modeled that addresses the factors listed above, then a MTBE concentration in a building's basement could be predicted (64). A key variable in such calculations is the initial ground-water concentration. For site-specific calculations, the actual ground-water concentration of the MTBE should obviously be used. If general predictive calculations are performed,

then a ground-water concentration should be used that accurately represents the plume being studied. Specifically:

<u>SUBSURFACE MTBE SOURCE</u>	<u>REPRESENTATIVE GROUND-WATER CONCENTRATION</u>
pure MTBE	42,000,000 µg/L or lower
tank-bottom water	9,700,000 µg/L or lower
MTBE-blended gasoline	100,000 µg/L. (236,000 µg/L is the highest recorded, but such a high level is quite rare)
wet precipitation	2 µg/L or lower

Based on data presented thus far, these are reasonable values for subsurface ground-water plumes if no measured values are available, but actual values should be used for a site whenever possible.

#### Gasoline Vapor Accumulation in Buildings - Field Experience

No literature citations were found regarding MTBE vapor measurements in basements. Historically, subsurface petroleum investigations have not typically measured for MTBE vapor accumulations. Some insight can be gained by summarizing field experience regarding gasoline vapor accumulation in buildings.

The author (Davidson) has dealt with approximately 300 gasoline spills. Of these approximately 15 have involved a reported vapor accumulation in a building. Without exception, all cases involved a building with a basement. This is logical as basements reduce the vertical separation between the building and the subsurface contamination, as well as providing a poorly ventilated accumulation area for vapors to collect. Vapor detections were typically first noted or suspected due to human detection. In some cases, proactive vapor detection steps were taken due to a building's position over a separate-phase gasoline layer.

Typically an emergency response was taken of measuring for gasoline vapors with a Flame Ionization Device (FID) or a Photo-Ionization Device (PID). In most cases (13 of 15 sites), no detectable vapors (detection limit of 1 ppbv) were noted in the buildings. Subsequently, the homeowner or building residents would not report any vapors, only to be followed some days, weeks or months later by another sudden report of vapor detection. This is very common and is likely due to rapid temporal fluctuations in subsurface vapor formation, vapor migration into the building, and vapor accumulation to detectable levels. All these variables will change rapidly based upon:

- barometric pressure changes
- daily (diurnal) temperature variations
- heating & ventilation practices of the building
- seasonal temperature variations
- water-table fluctuations
- additional contaminant releases

Repeated trips to a building (sometimes daily) with a FID or PID, inevitably led to many non-detects, followed sometimes by a later positive detection reported by the building residents. In order to overcome the problem of detecting rapidly changing vapor concentrations, automatic vapor detection equipment rigged to alarms were sometimes used. Alternately, long-term measurements can be obtained by installing carbon adsorption tubes that will provide a flux measurement of all volatile vapors. Sometimes the positive vapor reports would cease by themselves, but other times subsurface remediation of vapor-phase or dissolved-phase contamination was required to stop the positive vapor detections.

It is expected that if any MTBE vapors were to reach a basement, the detections would follow much the same pattern of being very sporadic, with only occasional positive readings. While this is difficult from a measurement perspective, it is beneficial from an exposure standpoint, as MTBE vapors would not be expected to be continuously entering a basement in most cases. As compared to the benzene vapor experience, factors that would promote MTBE vapor presence in basements include:

- higher possible MTBE concentrations in ground water (up to 200,000  $\mu\text{g/L}$ ) than benzene (typically maximum of 20,000 to 30,000  $\mu\text{g/L}$ ; see References 53 & 54)
- larger ground-water plume of MTBE (as described later, typically 1.5 to 2.0 times larger than the benzene plume)
- the longevity of MTBE due to its minimal biodegradation

Conversely, factors that would inhibit MTBE vapor presence in basements as compared to benzene would include:

- MTBE is less volatile from water than benzene
- the major portion of most MTBE ground-water plumes have concentrations less than 1,000  $\mu\text{g/L}$
- only about 30% of gasoline spills have MTBE in them
- since UST leaks are declining in number and size, less gasoline and less MTBE is being lost to the subsurface than previously.

#### Biodegradation of MTBE

MTBE is not expected to be readily biodegradable. Early work suggested this may be due to the resistance of the ether bond to microbial attack (65). Recent work (34) also suggested this, while an inability of MTBE to be transported into cells, or the lack of existing enzyme activities that can attack the ether bond, were also proposed.

Fujiwara et al. (39) reported that MTBE did not biodegrade well in the subsurface. As interpreted in a report by Environment Canada (45), Fujiwara et al. (39) provided biodegradation half-life estimates of 28 to 180 days for MTBE in aerobic soils and ground water although the method is unclear. This report (39) also provides estimates of 112 to 720 days for MTBE's half-life in anaerobic soils and ground water. However, it appears that the anaerobic estimates were simply mathematically assumed to be four times longer than the aerobic half-lives. All these biodegradation half-life values should be used with caution.

Bench-scale tests of soil and ground water (61) showed that after 232 days, there had been no measurable biodegradation of MTBE, even under an unlimited oxygen environment. In a limited

oxygen setting that more realistically modeled subsurface conditions of a gasoline release, no aerobic or anaerobic biodegradation of MTBE could be measured after 420 days. Another bench-scale test showed that after 182 days, there was no indication of anaerobic biodegradation of MTBE (36). A field scale study (61) showed that after 476 days essentially no MTBE mass had biodegraded from the ground water in a sandy aquifer. In general, MTBE does not biodegrade well under natural conditions.

There is some evidence to suggest that MTBE can biodegrade in the subsurface very slowly. The American Petroleum Institute (API) did find some MTBE mass loss (14%) after 476 days of monitoring a field study (61), however the loss was not clearly attributable to biodegradation. It is possible that some biodegradation may eventually occur, perhaps due to subsurface microbes adapting with time. Another report (37) showed that at one site impacted with MTBE and various hydrocarbons, after four weeks of aerobic incubation, 58% of the MTBE was apparently consumed by microbial degradation, although the evidence is limited. Recent laboratory analyses showed that MTBE can be aerobically biodegraded as evidenced by increased oxygen consumption rates (66).

Tests by ARCO Chemical Company (67) show that active sludges have the potential to biodegrade MTBE, especially when the sludges were already acclimated to the presence of MTBE. In another study, by collecting activated sludges from chemical plant biotreaters, a mixed bacterial culture was isolated and shown to biodegrade MTBE (34). After inoculation, enrichment and slow growth, the bacterial culture eventually was able to aerobically biodegrade 80-90% of the added MTBE, primarily to *t*-butyl alcohol (TBA). While these laboratory studies are not representative of most subsurface locales, they do demonstrate that aerobic degradation of MTBE is possible.

Similarly, anaerobic biodegradation of MTBE may also be possible. In one study, after an 84-day acclimation period butyl methyl ether (the straight chain analog of MTBE) began to anaerobically decay and convert to methane (36). However, the degradation rate was slow, and a tertiary carbon atom like MTBE would likely degrade much more slowly than an unbranched butyl methyl ether (36). Mormile et al. (68) found anaerobic degradation of MTBE to TBA in one of three replicate sediment samples collected from a locale exposed to repeated and varied fuel spills. Yeh and Novak (40) did report anaerobic (methanogenic) biodegradation of MTBE at one locale with low organic matter and a low pH of 5.5. This tentatively suggests that low pH may promote MTBE degradation.

It is also possible that sequential utilization governs substrate biodegradation (69). In studying biodegradation of TBA and methanol, it was seen that bacterial consumption of the less readily biodegradable TBA began only after the methanol had been consumed. While MTBE biodegradation in the subsurface is initially quite slow, this study suggests it might improve once more preferential carbon sources (ex: BTEX compounds) are consumed. This possibility is supported by work which showed ETBE was anaerobically biodegradable, but only when the more readily consumed ethanol was absent (40). Yeh and Novak (40) noted some anaerobic biodegradation of MTBE in soils where more readily degradable organics were absent (i.e. that contained low levels of naturally occurring carbon).

In summary, a few studies have noted direct evidence of MTBE biodegradation both aerobically (37, 67) and anaerobically (36, 40, 68). Acclimatization of the microbes (on a time frame of months to years) may promote slow biodegradation of MTBE (34, 40) as might low pH (40). Environments lacking more readily biodegradable carbon sources may be more likely to have MTBE biodegradation (40, 69).

### Discharge to Surface Water

Eventually, almost all ground water discharges to a surface water body (river, lake, bay, ocean etc.). As such, any MTBE in ground water will also discharge into a surface water body. Volatilization would then cause the MTBE to rapidly leave the surface water. The time until ground water reaches a surface water body varies greatly but is most likely years to tens of years for the shallow ground waters that might be impacted by MTBE.

### Other Mechanisms

While photooxidation is known to destroy MTBE (45), since the subsurface is essentially devoid of sunlight this process would not be significant for destroying MTBE in soils or ground water. Environment Canada (45) states that hydrolysis would not be effective as MTBE molecules have no hydrolyzable groups. Recent research (70) shows that no hydrolysis of MTBE occurs over a broad range of pH values (pH = 1-10). Reduction would not be expected to have any impact as there are no reducible groups in MTBE (45).

### Summary

For several reasons, MTBE contamination of ground water is usually limited to the uppermost portion of shallow aquifers. In some high organic content soils, adsorption may slow the forward movement of MTBE with the ground water and remove some MTBE mass. However, in general, adsorption is expected to have little effect and so dissolved-phase MTBE will move at the same rate as the ground water. Similarly, some minor biodegradation may occur in some aquifers, but MTBE reduction by this mechanism is generally minimal. The processes most likely to remove MTBE mass from the ground water are volatilization into the soil gas and volatilization into the atmosphere after the ground water discharges to surface water. Dispersion is an effective process for reducing MTBE concentrations in the ground water.

## EFFECTS OF MTBE UPON AROMATICS IN THE SUBSURFACE

### Reported Co-Solvency Field Experience

When dissolved into ground water, benzene is a *solute* and ground water is the *solvent*. There can be multiple solvents for a given solute. For instance, benzene (the solute) can dissolve into two different solvents - water and MTBE (52). If the second solvent is also present in ground water, it can cause the total solubility of the dissolving component in the ground water to increase. This solubility enhancement due to the presence of two solvents is known as *co-solvency*.

There have been reports in the literature (2, 71) of field experience that suggested MTBE can cause co-solvency of BTEX components. This suggests that the presence of MTBE might allow higher concentrations of BTEX in the ground water as well as increased BTEX mobility.

Garrett et al. (2) reported that in their experience, when no MTBE was blended into the fuel, total BTEX concentrations were often in the range of 10,000  $\mu\text{g/L}$  to 30,000  $\mu\text{g/L}$ . However, total BTEX concentrations up to 100,000  $\mu\text{g/L}$  are common based upon the author's field experience at hundreds of hydrocarbon sites, as well as published studies (53). Ground-water samples having total dissolved BTEX concentrations of greater than 100,000  $\mu\text{g/L}$  are almost always indicative of the presence of separate-phase gasoline product.

After studying a spill of gasoline blended with MTBE, Garrett et al. (2) reported that one well had 126,000  $\mu\text{g/L}$  of BTEX and MTBE combined. The gasoline-only concentration at this well was 40,474  $\mu\text{g/L}$ , which is well within the normal range for gasoline dissolved into ground water. This gasoline concentration is therefore not excessive, nor indicative of any co-solvency.

At this same spill site Garrett et al. (2) alleged that one well did show the effects of MTBE co-solvency. A water sample from shallow well 1-5 had a large gasoline and MTBE concentration (500,000  $\mu\text{g/L}$ ) with the gasoline components alone being 283,434  $\mu\text{g/L}$ . This gasoline value is indeed far above that normally associated with blended fuels, and initially may seem strongly indicative of MTBE's co-solvency potential. However, a review of Table 2 and Figure 4 of that report (2) clearly shows the sample was collected from a well within the separate-phase product plume. Similarly, at another site they report a record high of 600,000  $\mu\text{g/L}$  for BTEX and MTBE combined which suggests co-solvency is occurring (2). However, the sample collection description (Page 235 of Reference 2) clearly states that the sample was collected from directly beneath the separate-phase product.

Samples collected from wells containing separate-phase product do not provide meaningful dissolved-phase concentrations<sup>9</sup>. The concentrations measured are merely indicative of how much product was entrained or emulsified into the sample, but tell nothing about the actual solubility of BTEX or MTBE in the water itself. Therefore, it is concluded here that the 500,000  $\mu\text{g/L}$  and

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<sup>9</sup> It is nearly impossible to collect a water sample from a well with a floating separate-phase product layer without getting some globules of pure product in the water sample. The floating product gets smeared onto, and into, the sampling device when it is lowered down through the separate-phase layer in the well. Also, product is usually entrained or emulsified into the water sample during the bailing or pumping of the sample. For years, the common field practice has been not to sample ground water from monitoring wells that have separate-phase product because of this problem.



600,000  $\mu\text{g/L}$  samples are not representative, nor useful and are certainly not field evidence of MTBE induced co-solvency. Unfortunately, this was not recognized and the incorrect conclusion of MTBE causing co-solvency at this site has been referenced as key field evidence in the literature (44). In summary, while these reports (2, 71) were important and pioneering works regarding subsurface impacts due to oxygenate fuel additives, they in no way provide field evidence of subsurface co-solvency effects of MTBE. No other reports have been made with any field evidence of MTBE causing co-solvency.

#### Co-Solvency Experimentation

When reviewing reports regarding oxygenate co-solvency, the concentrations of oxygenate used in the study must be carefully compared to the amount of oxygenates used in actual fuels. For instance, Mihelic (72) reports that a 4.2% MTBE concentration in water caused an average 43% increase of aromatic hydrocarbon concentrations. Because MTBE is used in fuel at ranges up to 15% volume/volume, this may seem like MTBE can cause significant co-solvency. However, a careful review shows that Mihelic's MTBE percentages are in water, not fuel. A 4.2% MTBE concentration in water is equivalent to 42,000,000  $\mu\text{g/L}$  which is the maximum theoretical MTBE concentration that can be reached by pure (neat) MTBE. Thus this 43% solubility increase due to MTBE presence is only applicable in the very rare instances when pure MTBE has been released.

As demonstrated earlier, 15% MTBE in gasoline can produce a theoretical maximum of about 10,000,000  $\mu\text{g/L}$  (1% MTBE in water). Mihelic (72) shows that MTBE caused little to no solubility enhancement of aromatic hydrocarbons with MTBE at 1% in the water (10,000,000  $\mu\text{g/L}$ ). This level is roughly equivalent to the maximum theoretical and empirical concentrations of MTBE for blended gasoline tank-bottom waters (49) and may have some slight co-solvency effect there. However, no ground-water concentrations this high have ever been reported when the MTBE source is blended gasoline.

Mihelic (72) reports that 0.1 percent MTBE in water (1,000,000  $\mu\text{g/L}$ ) only increased aromatic hydrocarbon solubility by 1%. Therefore, even at the highest MTBE ground-water levels possible for a blended fuel spill, MTBE only causes a maximum 1% increase in aromatic hydrocarbon solubility. Such a 1% increase would not be noticeable within the range of aromatics normally seen in gasoline. Plots of aromatic solubilities (52) show that at the 0.1% (1,000,000  $\mu\text{g/L}$ ) MTBE concentrations seen in ground water, no measurable solubility increases exist.

Therefore, MTBE's presence in blended fuel at 10-15% volume/volume does not cause any measurable co-solvency effect to aromatic hydrocarbons dissolved into ground water. This conclusion is supported throughout the literature (50, 52, 72, 73). As correctly stated by Mihelic (72), even the highest MTBE concentration of 600,000  $\mu\text{g/L}$  reported by Garrett et al. (2) could not have caused significant solubility enhancement.

#### MTBE's Net Impacts Upon Aromatic Hydrocarbon Concentrations

Another key role of the MTBE is that it's addition dilutes the gasoline and lowers both the proportion and the volume of aromatics in the fuel (73). This reduces the aromatics available for dissolution into the water and suggests that BTEX concentrations should actually be lower in ground

water when MTBE is in the fuel. This is supported by another (52) study that showed that as the percent of MTBE in the fuel increased, benzene solubility in water decreased. API (73) also reports that a series of experiments showed BTEX concentrations did decrease as MTBE concentrations increased, specifically:

<u>% MTBE in fuel</u>	<u>Total BTEX (mg/L)</u>
0	122.8
5	115.4
10	114.0
15	107.4

Therefore, even if a worst-case 1% increase in solubility did occur due to some minor co-solvency effect of MTBE (as theorized by Mihelic (72)), this effect is more than offset by the reduction of BTEX components available for dissolution (73).

Because benzene's distribution coefficient was higher when MTBE was present, Cline et al. (50) predicted that benzene concentrations in water would be lower when 11% MTBE was in the water, than when no MTBE was present. The partition coefficient for the aromatics into the water appears to be about 5 to 10% less when 10% MTBE is in the gasoline. This was supported by two-phase solubility experiments (74) that showed MTBE concentrated in the oil phase and did not increase benzene solubility in the water. This effect enhances the net reduction of aromatic concentrations in the water due to MTBE's presence.

In summary, MTBE does not cause any co-solvency of aromatics (50, 72, 73). MTBE in gasoline actually reduces the aromatic concentrations in ground water for two reasons (50, 72, 73, 74). First, the MTBE substitutes for the use of high octane aromatics in gasoline. Second, MTBE will help retain the remaining aromatics in the bulk gasoline by providing a more soluble oil phase for the aromatics.

#### MTBE's Impacts Upon Biodegradation of Aromatic Hydrocarbons

The biodegradation of MTBE itself has already been discussed and shown to be non-existent to very slow in the subsurface. A review of MTBE's impacts upon the biodegradation of aromatic hydrocarbons is provided here.

The naturally occurring subsurface biodegradation of aromatic hydrocarbons is beneficial for contaminant reduction. There is concern that the presence of MTBE in the subsurface might somehow reduce, or inhibit, this beneficial biodegradation of the hydrocarbons. However, all available evidence demonstrates that MTBE's presence does not interfere with, or slow down, the biodegradation of hydrocarbon compounds.

As described in Garrett et al. (2) and Salanitro et al. (34), a paper by Fujiwara et al. (39) reported that the presence of MTBE (12% volume/volume in gasoline) had little effect on the biodegradability of the other gasoline components. In controlled laboratory and field studies, subsurface

mass loss rates of monoaromatics (i.e. BTEX) were not measurably different when 10% MTBE was added to the fuel (61).

The toxicity of MTBE does not appear to reduce or inhibit biodegradation of aromatics. Jensen and Arnn (35) found that various concentrations of MTBE in water up to 40,000  $\mu\text{g/L}$  had no inhibition effect, while 200,000  $\mu\text{g/L}$  of MTBE had a very weak inhibitory effect (o-xylene and m-xylene degradation were slowed by one day). Another study found that at 740,000  $\mu\text{g/L}$ , MTBE inhibited the biodegradation of some hydrocarbons (66). Studies conducted by ARCO Chemical Company (67) found that in a laboratory biodegradation study of MTBE only (no aromatics present) MTBE did biodegrade as evident by oxygen uptake by bacteria. The biodegradation of MTBE appeared inhibited when MTBE concentrations reached 1,700,000  $\mu\text{g/L}$ .

While the above referenced studies show that MTBE can cause inhibition, the dissolved MTBE concentrations required are quite high (200,000 - 1,700,000  $\mu\text{g/L}$ ). Such high MTBE concentrations very rarely occur in ground water (Table 15). Concentrations this high might occur only very near the source of a fuel spill (or in very rare instances, near tankbottom water releases or pure MTBE releases). This inhibition would likely be unimportant however, as the lack of dissolved oxygen normally encountered in such highly contaminated ground-water regions means that biodegradation of aromatics will be very slow anyway (75). As suggested by Table 15, most ground-water plumes will not have MTBE concentrations high enough (above 200,000  $\mu\text{g/L}$ ) to cause any inhibition of hydrocarbon biodegradation.

Because of its very low biodegradability, MTBE is not expected to use significant oxygen which might cause a reduction in the aerobic biodegradation of aromatics<sup>18</sup>. If, as preliminary evidence suggests, MTBE is found to be slightly degradable in the subsurface, then oxygen consumption by MTBE must be studied in further detail to determine any detrimental effects on aromatic degradation rates.

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<sup>18</sup> In contrast, methanol has been found to inhibit the biodegradation by two methods (51). Initially methanol inhibits biodegradation due to methanol toxicity, and then later by removal of oxygen due to preferential biodegradation over the aromatics.

## FIELD OBSERVATIONS OF MTBE & BTEX PLUMES

The author reviewed site assessment results from 30 Colorado locations that each had spills of MTBE-blended gasoline<sup>11</sup>. Based upon site records (inventory records, UST system testing, initially discovery of ground-water contamination, etc.), it appeared that it had been two to seven years since the fuel release at each of these 30 sites. As is typical with petroleum spill sites, the exact amount of fuel lost and the timing of the release (or releases) are not precisely known. In some cases, there was not even a measurable spill on record, and yet ground-water impacts existed.

At these 30 Colorado sites, it is likely that some spills contained as little as 6-8% MTBE (late-1980s octane enhanced fuel), while others had up to 15% MTBE (1990s oxyfuel). As is common, at these 30 sites multiple fuel releases of varying MTBE content probably occurred (including some non-MTBE containing fuel in the summer months), and the spill volumes and spill timing are not well known. As a result, it is not possible to determine precisely what the MTBE content was in the fuel spilled at these sites, or what the MTBE mass loss was that created the 30 ground-water plumes analyzed here. Unfortunately, this will be the case for almost all field sites. Only at intentional, controlled spills (61) and at a very few real-world facilities with excellent record keeping, would it be possible to correlate specific plume characteristics to particular MTBE percentages in fuel and spill volume. The 30 sites presented here therefore do not represent a particular spill scenario that can be mathematically correlated to ground-water plume conditions. Instead they represent a variety of MTBE volume loss scenarios and should be viewed as empirical information about MTBE plumes that form from blended gasoline spills.

There were 8 to 12 ground-water monitoring wells at each of these 30 sites and so experience from about 300 wells is summarized here (and listed in Table 15). Each well had been sampled sporadically for 4-7 years. The number of ground-water sampling events available for each site ranged between 6 and 12. Samples had been analyzed for BTEX and MTBE using USEPA 8020 or USEPA 602 Methods. Discussed below are a variety of observations made from this data.

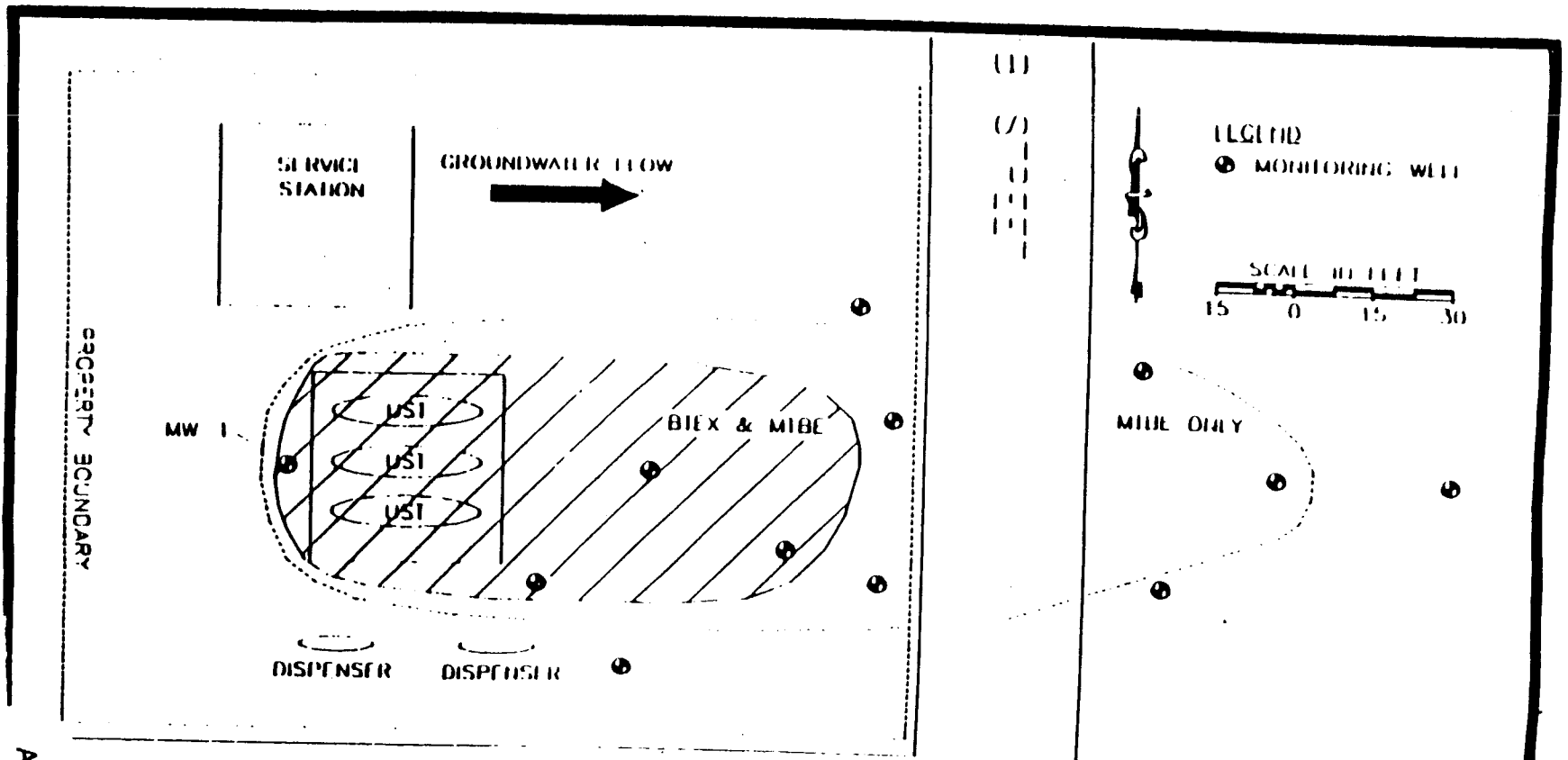
### Downgradient Extent of MTBE vs. Downgradient Extent of BTEX

In order to determine how much more extensive the MTBE ground-water plume was than the BTEX plume, maps were created of the lateral extent of the BTEX plume and the MTBE plume. The size of MTBE plume was defined by the projected contour of non-detect MTBE concentrations. The size of the BTEX plumes was represented as the projected non-detect contour for benzene as it is the fastest moving, and thus most extensive, aromatic hydrocarbon in ground water. Typically, the areal extent of the MTBE-only plume was 1.5 to 2.0 larger than the area impacted by benzene (Figure 5). No MTBE plume studied was more than twice the size of the associated benzene plume. Other spills and other locales may have different ratios.

This 1.5 to 2.0 MTBE:BTEX plume ratio was seen at another well-studied site. In the sandy, low-organic Borden aquifer (61) the MTBE had moved an average of 1.44 times further than the BTEX compounds after 106 days. By day 476, the MTBE had moved an average of 1.75 times further than the BTEX (see Table G-1 of Reference 61).

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<sup>11</sup> To protect site owner privacy, the site locations are not provided here.



### A SIRELI

ARC 063800

FIGURE 5. TYPICAL GROUNDWATER PLUME FROM A UST RELEASE SHOWING MIBE EXTENT IS TWICE AS GREAT AS BIEX EXTENT  
 NOTE: MW-1 HAS TRACE OF MIBE AND TRACE OF BENZENE, DUE TO SMALL SPILLS NEAR TANK PIT AND/OR SEPARATE UPGRADIENT SOURCE

DRAWN BY JAMES DAVIDSON  
 SEPTEMBER 12, 1995

This increase with time is logical as initially MTBE is able to outdistance BTEX components in the subsurface due primarily to the difference in their retardation (61). However, as the time since the fuel spill increases, natural biodegradation of the hydrocarbons should cause them to fall even further behind the MTBE which does not biodegrade well. This will cause the MTBE:BTEX plume ratio to increase with time.

Because the MTBE plume from a blended gasoline spill is often 1.5 to 2.0 times the size of the benzene plume, it is common to find positive detections of MTBE in a well, and yet no BTEX components. In such a scenario, the MTBE is most certainly due to the blended gasoline spill but MTBE may be the only component in approximately one third to one half of the ground-water plume (Figure 5).

#### High MTBE Detections Co-Occurred with High BTEX Values

As the MTBE concentrations varied spatially across the sites, the BTEX concentrations varied in the same manner. That is, where the highest MTBE concentrations were found the BTEX levels were also elevated. Also, as MTBE values fluctuated seasonally in a well over 4-7 years, the BTEX changed in a synchronous manner, although the absolute values of the MTBE concentration changes were not necessarily equal to the BTEX concentration changes. These significant seasonal variations of MTBE and BTEX concentrations means that time-series sampling wells is critical to understanding ground-water analytical data. A single sampling event is difficult to correctly and completely interpret by itself.

#### Cross-Gradient MTBE-only Detections

When wells are located on the lateral edge of the plume in a direction perpendicular to the ground-water flow, they are said to be *cross-gradient*. Field observations have shown that some cross-gradient wells can have MTBE concentration as high as 6.281  $\mu\text{g/L}$ , with very little BTEX or other hydrocarbons present. Another nearby well at the same site showed 4.400  $\mu\text{g/L}$  MTBE but only 4  $\mu\text{g/L}$  total BTEX.

This pattern occurs when the monitoring well is located just a short distance from the central mass of contamination, which produces a very steep concentration gradient. Because the non-retarded MTBE can reach the well through lateral dispersion, high MTBE levels reach can be found in the well. Even though the BTEX components would also have a steep concentration gradient, because they are retarded, these components do not quite reach the well. Only a few wells adjacent to the plume core will show such data trends.

### Highest MTBE Concentration Encountered

The single highest ground-water MTBE concentration seen by the author (Davidson) in any monitoring well at any site, was 200,000  $\mu\text{g/L}$  MTBE (as recorded in Table 15). The total BTEX in that sample was 26,000  $\mu\text{g/L}$ . That monitoring well was screened within, or immediately adjacent to, the backfill material in the tankpit where the leaking UST sat. The monitoring well consistently contained high BTEX and high MTBE values over 5 years; separate-phase product was detected in the well on several occasions. The other three tankpit monitoring wells surrounding the tanks had similar patterns and concentrations.

### Highest MTBE-only Detection in a Downgradient Well

One site had a monitoring well (MW-9) that was immediately downgradient of a known blended gasoline spill. MW-9 had a historical high of 879  $\mu\text{g/L}$  MTBE, with no BTEX detected (as recorded in Table 15). The maximum extent of benzene is located just 30 feet (9.1 m) upgradient of MW-9, as demonstrated by five years of monitoring data from a second well located 70 (21.3 m) feet upgradient of MW-9. Garrett et al. (2) report a well that had 690  $\mu\text{g/L}$  of MTBE but no BTEX. Depending upon the upgradient proximity of the BTEX plume, and upon the gasoline release conditions, it seems possible that higher MTBE concentrations might be encountered at other sites, even though no BTEX is simultaneously detected. However, it is almost certain that in such a case, BTEX and other hydrocarbons associated with spilled gasoline, are immediately upgradient of the MTBE plume.

Downgradient wells may have MTBE present as the only fuel-based contaminant for months or years. The existence of such MTBE-only wells is common, makes sense, and should be expected when reviewing ground-water analyses. As the BTEX components continue to migrate, some of the MTBE wells may eventually contain BTEX in the months or years to come. Benzene at low concentrations would be expected first, followed by increasing benzene levels, and then possibly followed by the gradual appearance of the more retarded, slower moving toluene, ethylbenzene and xylenes. If a well is further from the source than the hydrocarbons can extend (due to natural attenuation) than BTEX components may never reach that well, and it will remain impacted only by MTBE. This is commonly seen in downgradient wells.

Care must be taken not to interpret wells such as these as representing some MTBE-only source that is not related to a blended fuel spill. The hydrocarbons may or may not eventually reach the well, but spilled gasoline is definitely the source. Long-term, multi-event monitoring is desired for correctly interpreting such wells. As will be discussed later, depressed levels of dissolved oxygen in the ground water are an additional indicator of contamination due to fuel spillage. By combining dissolved oxygen monitoring data with MTBE occurrence, the spill source of a MTBE impacted well can be better identified. This will be discussed more in subsequent sections.

### Detection Patterns in Upgradient Wells

As expected, the majority of upgradient monitoring wells showed no MTBE detected the majority of the time. However, it was fairly common for an upgradient well to occasionally have a trace level detection of MTBE, with no BTEX. About one time out of twelve, an upgradient well would contain 2-310  $\mu\text{g/L}$  of MTBE, with no BTEX, and then have no further MTBE detections for several years. This occurred at numerous sites with no known spills in the immediate upgradient area, and apparently no off-site, upgradient MTBE sources nearby. These sporadic detections are considered to be either:

- false positives,
- upgradient dispersion of contaminants,
- remnants of small, unnoticed surface spills, or
- the very leading edge of an MTBE plume from another fuel spill that is considerably upgradient of the monitoring well.

These possibilities must be considered when interpreting ground-water analyses from upgradient wells.

### Highest MTBE-only Detection in an Upgradient Well

The highest MTBE-only detection noted in a well that was on the upgradient side of a site was 2,300  $\mu\text{g/L}$ . However, this well was downgradient of another UST site with known leaks. The MTBE concentrations remained consistently positive and elevated, but no BTEX appeared in the well over the course of 4 years. This is typical of a well that is upgradient of the site monitored, and yet downgradient of another source. The upgradient source readily explains the high MTBE-only detection. The BTEX components may/may not eventually appear in such wells. While the 2,300  $\mu\text{g/L}$  was the highest such MTBE concentration noted, several other sites also had "upgradient" monitoring wells with MTBE at 10-1,000  $\mu\text{g/L}$ , with no BTEX detected. This shows the importance of conducting repeated ground-water sampling with time (so such trends can be detected) and the need for considering upgradient landuse (so other MTBE sources can be identified). Conducting single sampling events and not considering other upgradient sources, can lead to incorrect interpretations of the limited data.



## MTBE IN WATER SUPPLY WELLS

### MTBE Odor and Taste Thresholds

Because MTBE is not retarded onto soil organic matter, it moves at essentially the same rate as the ground water (61). The aromatic hydrocarbons associated with gasoline spills are retarded to varying degrees and so they move slower than the ground water (61). As such, MTBE will be the first contaminant to reach a well or particular point in the aquifer due to a MTBE-blended gasoline spill. The detection of MTBE in a well provides notice that more toxic components (ex. benzene) associated with blended gasoline spills are forthcoming (2).

MTBE in water has a low odor detection threshold of 45  $\mu\text{g/L}$  in water and a low taste threshold in water<sup>12</sup> of 39  $\mu\text{g/L}$  (7). As a result, it can be readily detected by humans and so the offensive taste and odor of MTBE will warn a wellowner about subsurface contamination before the arrival of the more toxic components like benzene and other aromatics. In one case, users of an MTBE-impacted water supply complained of undesirable taste and odors when MTBE concentrations were as low as 5 to 15  $\mu\text{g/L}$  (1). MTBE can thus act as a subsurface "early warning" system that helps prevent consumption of higher MTBE concentrations and the more toxic BTEX compounds (77).

### Detection Methods

MTBE, along with other VOCs, can be measured in water supply wells by collecting water samples and analyzing them by numerous standard methods such as EPA Methods 524.2 or 502. MTBE can be analyzed for in public water supplies at little to no cost because it can be quantified during VOC analyses already required. Monitoring for alcohol-based oxygenates would require additional, non-standard analyses to be conducted at additional expense.

### Concentrations Encountered

An extensive effort was made by the author to collect all available data regarding MTBE concentrations in public and private water supplies. Multiple state agencies were contacted and the results are compiled in Tables 18 and 19. Appendix E contains a discussion of data collection methods, data quality, and uncertainty. While this dataset does not include all 50 states, it is one of the most complete available and will be used here to establish the concentrations of MTBE typically found in public and private water supply wells.

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<sup>12</sup> Odor detection threshold and taste detection thresholds are the lowest levels that panelists could first detect MTBE presence when it was the only component present. These are appropriate to use when considering detection of MTBE-only in a water supply well as MTBE will be the only component present when it first reaches a well through migration with the ground water. Values vary in the literature; the values reported here are the average values reported in an API study (Reference 7). Individual responses are expected to vary.

**TABLE 18 - MTBE OCCURRENCE IN PUBLIC WATER SUPPLIES (NOTE 1)**

STATE	YEARS OF REPORTED DATA	TYPE & # SYSTEMS TESTED	# OF SYSTEMS W/MTBE	DUE TO LOCAL SPIKE	# WELLS UNKNOWN SOURCE	DEFECT TIME (ug/l)	# OF NON-DEFECTS	# OF MTBE < 10 ug/l	# OF MTBE 10-20 ug/l	# OF MTBE 20-200 ug/l	# OF MTBE > 200 ug/l	REFERENCES
ILLINOIS	1990-95	mixed, 1070	GW - 7	5	2	0.5	1023	3	0	3	1	78
MASSACHUSETTS	1991-94	mixed, 10	GW - 1	?	?	0.5	27	1	0	0	0	79
NEW YORK	1993-94	GW - 3	0	NA	NA	0.2	3	0	0	0	0	USGS NAWQA
NEW JERSEY	1989-93	mixed, 610*	mixed, 59*	?	?	0.5	571	57	1	1	0	80
WISCONSIN	1995	GW - 4	0	NA	NA	5	4	0	0	0	0	81
WISCONSIN	1995	SW - 2	0	NA	NA	5	2	0	0	0	0	81

<b>TOTALS</b>		2499	69	7	7	-	2430	63	1	4	1	
<b>PERCENTS</b>		100.00%	2.76%	?	?	-	97.24%	2.52%	0.04%	0.16%	0.04%	

**TABLE 19 - MTBE OCCURRENCE IN PRIVATE GROUND WATER WELLS (NOTE 1)**

STATE	YEARS OF REPORTED DATA	# WELLS TESTED	# WELLS W/MTBE	DUE TO LOCAL SPIKE	# WELLS UNKNOWN SOURCE	DEFECT TIME (ug/l)	# OF NON-DEFECTS	# OF MTBE < 10 ug/l	# OF MTBE 10-20 ug/l	# OF MTBE 20-200 ug/l	# OF MTBE > 200 ug/l	REFERENCES
GEORGIA	1991-94	2	0	NA	NA	0.2	2	0	0	0	0	USGS NAWQA
MINNESOTA	1991	67	1	?	?	2	67	0	0	1	0	STORET (NOTE 2)
NEW JERSEY	1989-93	approx 650*	65	?	?	0.5	585	45*	13*	6*	1*	80
NEW MEXICO	1991	22	0	0	0	5	21	0	0	0	0	STORET (NOTE 2)
WISCONSIN	1992-95	350	9	9	0	5	341	0	2	4	1	81

<b>TOTALS</b>		1291	69	7	7	-	1216	45	15	11	4	
<b>PERCENTS</b>		100.00%	5.34%	?	?	-	94.19%	3.49%	1.16%	0.85%	0.31%	

(NOTE 1) These state data sets are typically non-complete (not every public or private well tested) and non-continuous (not all wells tested every year or every event), but are best available.

(NOTE 2) This STORET data is apparently all from private ground-water supply wells, although this could not be verified with the data collector.

**Explanation:**

- mixed - ground water supplies and surface water supplies, percentages unknown
- GW - ground water system
- SW - surface water system
- ? - unknown, can not be determined with available data
- \* - extrapolation made by dividing known amount upon raw data from NAWQA MS10W
- NA - not applicable

It is useful to compare MTBE ground-water concentrations seen in water supply wells (Tables 18 and 19) to the levels created by MTBE dissolved into wet precipitation. The concentrations of MTBE in water supply wells are 1 to 2 orders of magnitude (i.e. 10 to 100 times) greater than the ground-water concentrations of MTBE that might result from wet precipitation (maximum = 2 µg/L).

Considering the limited ground-water MTBE concentrations that can form from wet precipitation (maximum of about 2 µg/L), and also considering the concentration reducing effects of volatilization, dilution while pumping, and water source blending, it is clear that essentially none of the water supply wells (either public or private) have been impacted by MTBE that came from wet precipitation. Any MTBE concentrations greater than 2 µg/L in water supply wells must be due to local point source releases of MTBE-blended gasoline.

The MTBE concentrations seen in public and private ground water supplies (Tables 18 & 19) are typically 1 to 3 orders of magnitude (10 to 1,000 times) lower than those encountered in ground water near point source releases of MTBE blended fuel (Table 15). This is because most of the analyses in Table 15 are from monitoring wells intentionally located near the spill sources. In contrast, water supply wells are usually further away from the spills, and are often screened deeper, both of which reduce the concentrations encountered. Additionally, when water supply wells operate they extract large volumes of water which dilutes the MTBE concentrations. These concentration reducing processes are discussed in greater detail below.

The highest MTBE concentration in a public drinking water well discovered was 770 µg/L (78). The highest MTBE concentrations reported for private water wells (Table 19) is a well in New Jersey that had 800 µg/L MTBE (80). Another study (55) reported 987 µg/L in a private water-supply well. In contrast, ground-water plumes from point source releases often have MTBE levels of 10 to 100,000 µg/L; the highest MTBE concentration seen in the ground water was 236,250 µg/L.

In summary, MTBE concentrations seen in water supply wells are significantly higher than could be produced from MTBE dissolved into wet precipitation or stormwater runoff. Conversely, MTBE concentrations in water supply wells are significantly lower than levels seen near local point source plumes formed by blended gasoline releases.

It is important to note that while certain water supply wells have MTBE concentrations that exceed recommended guidelines for consumption (e.g. greater than 200 µg/L), the water from such wells will usually not be consumed because:

- MTBE's low odor and taste thresholds act as a warning not to consume the water, and as a trigger event to begin subsurface investigations;
- any water supply wells with MTBE concentrations at this level are attributable to local point source releases of MTBE-blended gasoline. As such, MTBE concentrations above 200 µg/L almost always co-occur with elevated BTEX concentrations, thus providing more warning signs that will prompt investigation and stop consumption. In public supplies BTEX compounds are regularly monitored;
- cessation of using the impacted well, or adding treatment systems (like activated carbon or aeration) are the typical response.

## Regulatory Levels

Listed in Table 20 are some suggested and enforceable action levels for MTBE in drinking water supplies (i.e. they are health based). Some of these are state-specific and were calculated by regulatory bodies, while the last two are generic health-based levels determined by non-government organizations.

TABLE 20  
SOME REGULATORY LEVELS FOR MTBE IN DRINKING WATER

APPLICABLE IN	MTBE CONC. ( $\mu\text{g/L}$ )	TYPE OF STANDARD	REFERENCE
ILLINOIS	230	HUMAN THRESHOLD TOXICANT ADVISORY CONCENTRATION	82
NEW JERSEY	70	MAXIMUM CONTAMINANT LEVEL	83
MAINE	50	DRINKING WATER THRESHOLD	84
WISCONSIN	60	GROUND WATER ENFORCEMENT STANDARD	81
GENERIC VALUE BY KLAN & CARPENTER	200	DRINKING WATER LEVEL FOR HUMAN HEALTH PROTECTION	85
GENERIC VALUE BY CALABRESE & GILBERT	220	DRINKING WATER LEVEL FOR HUMAN HEALTH PROTECTION	85

Not all regulatory levels in existence are provided here as this information is in a state of flux. For instance, other regulated values may exist for: Connecticut, Delaware, New Hampshire, Florida, Massachusetts, Michigan, North Carolina, or other states.

## Conditions that Reduce MTBE Concentrations in Water Supply Wells

As discussed, MTBE plumes in ground water are often 1 to 3 orders of magnitude higher than the concentrations encountered in water supply wells. Because water supply wells extract ground water, there must be several factors to explain these differences; these are discussed below.

### Spatial Separation

Based on extensive field experience investigating hydrocarbon spills, it is unusual to find a public water supply well near a service station or other petroleum handling facility. This is logical as wellhead protection practices act to avoid having possible contaminant sources near water supply wells. Also, the most common gasoline handling facilities are service stations and they occur most often in urban areas. These urban areas are usually served by public water systems that have their wells located away from the population centers (a demographic form of wellhead protection).

Spatial separation of gasoline sources and water supply wells would be less in rural areas as service stations will often be located near the small community. In rural areas, public water supplies may not be drilled as deep, nor have their wellheads protected and isolated as well due to lack of municipal funding. Small communities are also more likely to have private water wells that may have even less spatial separation away from service stations. These are contributing factors that might explain the higher incidence of MTBE in private wells (Table 19) than in public wells.

### Geologic Separation

As gasoline and MTBE both have specific gravities less than water, contamination by these compounds will not sink downward to deeper units, unless atypical flow conditions exist (i.e., downward vertical flow). As discussed, while vertical dispersion will slightly spread MTBE downward over time, this should be minimal. Because of these factors, and because of MTBE release mechanisms, MTBE contamination should primarily occur in the shallowest, first encountered, water-saturated units.

In contrast, many public supply wells (but not all) are screened across completely different, and much deeper aquifers than the first encountered water-bearing units typically impacted with MTBE and hydrocarbons. Therefore, a vertical, stratigraphic separation often exists between shallow MTBE impacted aquifers and the deeper water supply aquifers from which many public water supply wells pump. Such a geologic separation barrier helps keep shallow, impacted ground water away from deeper public water supply aquifers. Again, this form of protection would be less likely for private wells which are not typically drilled as deeply as public wells.

Depending upon the well construction, water withdrawal rate and local hydrogeology, even if geologic separation does exist, some water from a contaminated shallow unit may be drawn down into a deeper unit and impact a water supply well (48). Also, both private and public water supplies can be withdrawn from shallow aquifers in some areas, and so MTBE and aromatic contamination of wells will occasionally occur (2).

#### Dilution During Water Removal

The high extraction rates associated with public water systems means that if any MTBE were present in the influent water, it should be significantly diluted. By design, and due to the large extraction rates needed (typically 50 - 1,000 gallons per minute (189-3,785 liters per minute)), public supply wells usually have large screened zones and withdraw water from large thicknesses of aquifers. If a public supply well were impacted with MTBE, since the influent water comes from a large vertical portion of the aquifer, but the MTBE is typically found in only the shallowest portions of the aquifer, there would be significant dilution effect. This is due to deeper, non-MTBE containing water diluting the shallower, MTBE-impacted water. Such dilution would be expected to reduce MTBE concentrations.

This effect is commonly seen in ground-water remediation projects. Shallowly screened monitoring wells near MTBE-blended gasoline spills may have high concentrations of MTBE. However, when deeper-screened recovery wells extract large volumes of ground water from larger portions of the same aquifers, the average MTBE concentration in the extracted water is often 1-2 orders of magnitude lower (i.e. diluted).

#### Dilution by Blending

Many public water systems have several streams of water influent that are blended to produce the final supplied-water stream. If one well or surface water body in the mix were impacted by MTBE, then the total MTBE concentration would be diluted according to the mixture ratios at the individual facility. This multi-source dilution would not be applicable for a public system that used a single source for its water, but such circumstances are unusual.

#### Summary

As discussed, there are several inherent factors that help prevent local elevated MTBE concentrations in ground water from appearing in drinking-water wells. These factors include:

- spatial separation of water supply wells from contamination
- geologic separation of shallow, contaminated units from deeper water-supply aquifers
- dilution during water withdrawal
- dilution due to water source blending
- volatilization of MTBE at several stages

All these factors provide beneficial reduction of MTBE concentrations in water supplies. Fortunately, contamination of water-supply wells by MTBE is not common (Table 18).

## Reduction of MTBE Concentrations by Public Water Supply Treatment Systems

If the above discussed inherent factors do not completely prevent MTBE from reaching a water supply well, the water supply treatment system may further reduce the MTBE concentrations received by the water users. MTBE removal due to the normal operations of a public water supply treatment system has not been well studied or reported in the literature. Also, the type of treatment systems used varies widely depending upon the water source (surface water and/or ground water) as well as the ambient water chemistry. Therefore, it is difficult to quantify the impacts of standard treatment operations upon MTBE concentrations. However, by reviewing the processes commonly used at water treatment facilities, it can be seen that MTBE reductions are inherently expected.

### Aeration

No references were found regarding the aeration effects of normal pre-treatment procedures upon MTBE or VOC concentrations. However, some insight can be gained by reviewing effects of other aeration procedures.

Malley et al. (55) reported on point-of-entry treatment systems for ten private household water supplies impacted by MTBE from blended gasoline soils. They found treatment by bubble plate aeration (volumetric air to water ratio of 150:1) reduced MTBE concentrations an average of 60%. A field study of fifteen ground-water remediation projects (43) reported 55.6% to 99.9% removal rates for MTBE by aeration via packed columns (volumetric air to water ratios ranging from 1:1 up to 47:1).

After reviewing several years of operating data from air stripping systems, the NJDEP (80) reported that air stripping with a single tray aerator (air to water ratio of 120:1) removed 50% to 60% of MTBE present. A laboratory scale study (86) showed that aerating one gallon (3.785 liters) of water for 120 minutes with an air:water ratio of 35:1 reduced MTBE concentrations 60% (from 1.2 mg/L to 0.480 mg/L).

Two other publications (44, 87) both describe results from a series of analyses and bench scale tests performed for API to determine the feasibility and cost-effectiveness of removing MTBE from ground water. A series of six aeration tanks were found to be half as cost-effective at removing high concentrations of MTBE (from 20 mg/L down to 0.010 mg/L) as compared to the more effective technique of aeration via packed air-stripping columns.

Aeration by bubble plate, packed column, or multiple batch tank methods are likely to be more effective than the aeration techniques typically employed at water pre-treatment plants. However, considering these studies, as well as MTBE's strong ability to volatilize rapidly, water supply pre-treatment aeration may have the potential to remove approximately 50% of MTBE, depending upon air to water ratios and methods used. Specific analysis of MTBE removal capacity for the aeration procedures typically used at water supply facilities would be needed to provide additional supporting data and to further refine this initial estimate.

### Oxidation

Where already applied as part of a water supply's pre-treatment process, oxidation should also provide beneficial reduction of MTBE. No studies were found discussing the MTBE removal using the oxidation techniques specific to water pre-treatment. However, oxidation by ozone or ultra-violet light would provide beneficial MTBE reductions (44), although the percentages are not currently quantifiable.

### Other Pre-Treatment Processes

The common process of filtration through sand beds could also reduce MTBE concentrations somewhat due to the volatilization that occurs as the water trickles downward through the sand bed. The sand itself provides little benefit in removing, retaining, or destroying MTBE.

Filtration through a granulated activated carbon (GAC) bed would provide very efficient, but short-lived removal of MTBE. Malley et al. (55) report that GAC beds can remove greater than 90% of MTBE present while another study showed an 87% MTBE removal rate at one site (43). However, since MTBE adsorbs to organic matter and GAC quite poorly it typically "breaks through" GAC treatment units rapidly (1, 55). Therefore, MTBE would be expected to breakthrough a typical water treatment plant GAC bed very quickly (perhaps weeks to months). Such breakthrough could only be avoided if the presence of MTBE was known to the water supplier, and the GAC was replenished with new GAC on more frequent intervals than is common for water treatment plants.

Other common water treatment processes include chlorination, coagulation and sedimentation. The presence of chlorine is not anticipated to impact MTBE concentrations, nor should the processes of coagulation or sedimentation. MTBE is not expected to promote the formation of trihalomethanes in chlorinated water supplies as the chlorine should preferentially react with other, more active organic matter and not MTBE. No pertinent studies were found in the literature that addressed MTBE's interactions with these processes.

### Number of Public Water-Supply Wells Contaminated with MTBE above Action Levels vs. Number of MTBE-Blended Gasoline Releases

The role of the above discussed factors in protecting public water-supply wells can be demonstrated by comparing the number of public water-supply wells that have been contaminated with MTBE above action levels against the number of MTBE-blended fuel releases.

### Wells with MTBE Exceedances

Since complete national information regarding MTBE concentrations in public water supply wells is not available, two states will be used in the calculations. The public water supply wells in New Jersey and Illinois are used as they have the most comprehensive public water-supply database for MTBE analysis. Both New Jersey and Illinois have regions with numerous public and private water supplies from shallow aquifers which provides "worst-case" projections. Additionally, New Jersey represents a state with "worst case" MTBE releases due to its long-term use (since the early 1980s)



and wide-spread use (most of the state) of MTBE. Illinois uses more ethanol as a gasoline additive than MTBE and so Illinois is a state with minimal MTBE use.

Based on the regulatory levels listed in Table 20, this analysis will use action levels of 200 µg/L of MTBE to represent a common action level, and 50 µg/L of MTBE to provide a very conservative action level. By reviewing Tables 18 and 19, as well as the original references for these analyses (80, 78), it can be seen that:

- 3 public wells exceeded 50 µg/L (3 sites in Illinois)
- 1 public well exceeded 200 µg/L (Illinois)

No public wells in New Jersey exceeded either action level; one Township had a record high MTBE concentration of 47.5 µg/L (80).

#### Number of MTBE-Blended Fuel Releases

The number of UST spills that involved MTBE blended gasoline could be most precisely estimated by doing a time-weighted average of how many tanks were found to be leaking in which year, and multiplying those values against how much of the gasoline sold in each state, in each year, had MTBE. Unfortunately, state-specific values of how much MTBE was used in each year, in each state were not available. Also, determining how many tanks leaked in each year in each state would require extensive state file reviews, and would rely upon reported release dates that are usually unreliable. Therefore, this was not conducted.

As a result, a generalized approach is used here by applying national statistics to these two states. As shown in Table 1, MTBE was in 4% of the nation's gasoline in 1980, 10% in 1985, 18% in 1990 and 29% in 1995. Many leaking USTs were discovered in the 1980s and early 1990s, while the rate of new leak discoveries was declining (Table 16 & 17). As such, using MTBE in gasoline percentages from only 1980, 1985 and 1990 (and ignoring 1995) probably more accurately represents the number of tanks that leaked MTBE-blended fuel. However, in order to be conservative 1995 values will be included, and so an overall mean of 15% (the mean of 4% + 10% + 18% + 29% = 15.25%) will be used to represent how many tanks leaked MTBE-blended fuel.

As of August 1995, Illinois and New Jersey report 12,930 releases and 5,627 releases respectively (88). Therefore, the total number of UST releases in these two states is 18,557. Since about 15% of these USTs may have contained MTBE-blended gasoline between 1980-1995, approximately 2,784 releases may have occurred that contained MTBE-blended gasoline.

#### Summary

Of 2,784 MTBE-containing gasoline releases in New Jersey and Illinois, only 3 apparently produced MTBE concentrations in a public drinking water well greater than 50 µg/L. Only one release of the 2,784 caused MTBE concentrations in a public well to exceed 200 µg/L in these two states. While these calculations are generalized, it is apparent that multiple factors act to prevent MTBE-blended gasoline spills from impacting public water supplies.

## USGS NAWQA STUDY

### The USGS NAWQA Program

In 1991 the United States Geological Survey (USGS) began conducting a national survey of ground-water quality under the National Water-Quality Assessment (NAWQA) program (89). In the recently completed Phase 1 of the program, eight urban areas and twenty-two agricultural areas were studied (30). During 1993-1994, ground-water samples were collected from 211 shallow wells and springs in urban areas and 562 shallow monitoring wells in agricultural areas (30, 48). In addition, 413 deeper wells in nine Study Units were also sampled (48). Therefore, the USGS has data regarding MTBE occurrence in a total of 1,186 ground-water sampling points<sup>13</sup> (30, 48, 90).

Of the 211 shallow urban sampling locales, 5 were drinking-water wells<sup>14</sup>, 194 were monitoring wells, and 12 were springs. The information reported here about the techniques, analytical methods, and findings was collected from a USGS Open File Report (48), brief published data sheets (30, 90), raw data requests, and direct contact with the USGS NAWQA personnel.

### Well Selection Criteria

The well selection criteria for the 413 wells in the nine deeper aquifer study areas is unknown (48). Based upon conversations with USGS personnel, the following well selection criteria were apparently used in each of the eight urban and twenty-two agricultural shallow study areas:

- each study area was broken into hundreds to thousands of smaller sub-units and assigned a number
- within each study area, by using a USGS random number generator, 15-45 subunits were randomly selected for ground-water sampling.
- for each selected subunit, existing public records were reviewed in an attempt to find shallow wells of "high quality" (i.e. detailed well construction information, thorough drill logs, good seals, appropriate well screening intervals, appropriate well construction techniques and materials, etc.).
- these wells, or other existing wells found by visiting the subunit of interest, were then sampled.

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<sup>13</sup> The USGS provide NAWQA project identification numbers and latitude and longitude values for well identification purposes. The exact locations (address, owners) are not available to protect individual privacy.

<sup>14</sup> Although initial reports (30, 91) stated that no drinking water wells were sampled, a USGS review of the database conducted in the summer of 1995 revealed that five (5) of the sampled wells were in fact drinking water supply wells (48). Two were domestic water supply wells in Georgia (USGS study area ACFB) and three were public supply wells in New York (USGS study area HDSN).

While this process started out randomly selecting wells for sampling, the "high quality" well requirements introduced bias into the well selection program, especially in the urban study areas. Because only newer (primarily 1980s & 1990s) monitoring wells can meet the well design quality criteria, the well selection program is biased towards newer monitoring wells. One of the primary reasons for installing shallow monitoring wells since the mid-1980s is to look for, and identify the extent of, ground-water pollution. A common site likely to be studied for ground-water contamination is a facility with gasoline USTs, especially in urban areas.

As a result, the well selection criteria skewed the database more towards sampling monitoring wells that are near USTs, and thus near gasoline leaks. Therefore, the database itself is biased towards identifying local point sources of MTBE and hydrocarbons, as opposed to a true random dataset. As service stations are very commonly investigated in urban areas, this well selection bias is strongest in the eight urban study areas.

Discussions with USGS personnel indicate that there was partial recognition of this bias. Therefore, when multiple monitoring wells were available at a selected sampling locale, a well on the upgradient side of a site was sampled when the ground-water flow direction was known. However, demographics and marketing techniques dictate that service stations often occur in clusters (e.g. two or more at an intersection). As a result, even though ground-water samples may have been collected from a monitoring well on the upgradient side of one service station, that well may still be downgradient of an adjacent UST. This means that the bias towards sampling wells more likely to be impacted with hydrocarbons and MTBE was not avoided by sampling "upgradient" wells. This factor is amplified for MTBE as the MTBE plumes can be 1.5 to 2.0 times as large as the BTEX plumes. As a result, when selecting wells for sampling on the assumption that they are away from all point sources (as was described by the USGS in Reference 48), it is still possible to sample a well that is impacted by a MTBE-only plume, while erroneously believing that the well is away from all point source plumes.

Even if no other service station existed upgradient of the sampled well a bias towards sampling gasoline-impacted wells still exists. Field experience at hundreds of service stations shows that it is not at all unusual to have traces of gasoline contamination, including dissolved-phase MTBE, in the wells on the upgradient side of a site. This can be caused by:

- previously unknown small fuel spills
- variable ground-water flow directions
- dispersion from the on-site plume
- dispersion from off-site, cross-gradient plumes

As previously discussed, the author's experience has been that finding dissolved-phase MTBE in upgradient monitoring wells is not uncommon in urbanized areas. The authors of this report therefore maintain that for these reasons, the USGS NAWQA program appears to be biased towards sampling wells likely to be located near UST facilities (especially in urban areas) and wells that may be impacted by MTBE only. Within the urban setting, this bias should be greatest in the industrial landuse areas, less so in commercial areas, and least in residential areas. As a result, the sampled wells are more likely to detect MTBE and hydrocarbons than shallow wells that were truly selected at random. Additionally, many of the MTBE occurrences detected in these 8 urban, shallow study units are likely to be local point source plumes from USTs. Supplementary data to support this contention is presented below.

### Analytical Procedures

For each sample collected, approximately 180-200 different compounds were quantified including 60 VOCs like MTBE, benzene, toluene, ethylbenzene and xylenes. All samples were analyzed at the USGS National Water-Quality Laboratory in Arvada, Colorado. VOCs were analyzed by a slight USGS adaptation of USEPA Method 524.2 which is a purge and trap technique for drinking water analysis (92). The detection limit for MTBE, benzene, toluene, ethylbenzene and the three xylenes was 0.2 µg/L. This is 2.5 to 5.0 times lower than most commercial laboratories.

### Findings

Tables 21 and 22 provide summary statistics for twenty agricultural areas and the eight urban areas, respectively. Table 21 only has detailed information on 523 of the 562 agricultural wells (in twenty of the twenty-two study areas) at that was all that was available at the time of this report. Some key findings regarding the MTBE occurrence detected by Phase 1 of the USGS NAWQA study are contained in Table 23. Appendix F provides the analytical results for all 211 urban wells and springs for the parameters of MTBE, BTEX and dissolved oxygen. Squillace et al. (30) provide a broad overview of the MTBE findings, as does a brief article in *Ground Water Monitoring & Remediation* (91). The recent Open File Report (48) provides more detailed information, including the data on the 413 deeper wells, the two additional agricultural study units, and the stormwater runoff sampling.

TABLE 21 - MTBE OCCURRENCE IN SHALLOW AGRICULTURAL GROUND WATER, USGS NAWQA PHASE I

STATE	YEARS (IF REPORTED DATA)	# WELLS TESTED	# WELLS W/MTBE	LIKELY LOCAL SOURCE	LIKELY NONPOINT SOURCE	DETECT LIMIT (ug/L)	# OF NON-DETECTS	# OF MTBE < 10ug/L	# OF MTBE 10-20ug/L	# OF MTBE 20-200ug/L	# OF MTBE > 200ug/L	REFERENCES
APPALACHIAN	1993	32	0	0	0	0.2	32	0	0	0	0	USGS NAWQA
ALBEMARLE-PAMUNCE	1994	20	0	0	0	0.2	20	0	0	0	0	USGS NAWQA
CENTRAL COLUMBIA	1993-94	45	0	0	0	0.2	45	0	0	0	0	USGS NAWQA
CENTRAL COLUMBIA	1993-94	21	0	0	0	0.2	21	0	0	0	0	USGS NAWQA
NEW ENGLAND	1993-94	22	2	0	2	0.2	20	2	0	0	0	USGS NAWQA
ETA-GEORGIA	1994	23	0	0	0	0.2	23	0	0	0	0	USGS NAWQA
LOW SUSQUEHANNA	1993	30	4	0	4	0.2	26	4	0	0	0	USGS NAWQA
POTOMAC	1993	17	0	0	0	0.2	17	0	0	0	0	USGS NAWQA
RIO GRANDE 1	1994	20	0	0	0	0.2	20	0	0	0	0	USGS NAWQA
RIO GRANDE 2	1993	35	1	0	1	0.2	34	1	0	0	0	USGS NAWQA
SAN JOAQUIN 1	1993-94	20	0	0	0	0.2	20	0	0	0	0	USGS NAWQA
SAN JOAQUIN 2	1994	20	0	0	0	0.2	20	0	0	0	0	USGS NAWQA
SOUTH PLATTE	1994	30	0	0	0	0.2	30	0	0	0	0	USGS NAWQA
UPPER SNAKE 1	1993	31	0	0	0	0.2	31	0	0	0	0	USGS NAWQA
UPPER SNAKE 2	1993	28	0	0	0	0.2	28	0	0	0	0	USGS NAWQA
UPPER SNAKE 3	1994	30	0	0	0	0.2	30	0	0	0	0	USGS NAWQA
WILLAMETTE 1	1993	15	0	0	0	0.2	15	0	0	0	0	USGS NAWQA
WILLAMETTE 2	1993	26	0	0	0	0.2	26	0	0	0	0	USGS NAWQA
WEST LAKE MICHIGAN 1	1993-94	28	0	0	0	0.2	28	0	0	0	0	USGS NAWQA
WEST LAKE MICHIGAN 2	1994	30	0	0	0	0.2	30	0	0	0	0	USGS NAWQA
TOTALS		523	7	0	7	-	516	7	0	0	0	
PERCENTS		100.00%	1.34%	0.00%	1.34%	-	98.66%	1.34%	0.00%	0.00%	0.00%	

Explanation:

7 - unknown, can not be determined with available data

+ - local source identified by presence of benzene, toluene, xylene, ethylbenzene, and/or by DO less than 2.0 mg/L.

NA - not applicable

TABLE 22 - MTBE OCCURRENCE IN SHALLOW URBAN GROUND WATER, USGS NAWQA PHASE I

STATE	YEARS OF REPORTED DATA	# WELLS TESTED	# WELLS W/MTBE	LIKELY LOCAL SOURCE	LIKELY NONPOINT SOURCE	DETECT LIMIT (ug/L)	# OF NON-DETECTS	# OF MTBE < 10ug/L	# OF MTBE 10-20ug/L	# OF MTBE 20-200ug/L	# OF MTBE > 200ug/L	REFERENCES
ATLANTA	1994	23	2	1	1	0.2	21	2	0	0	0	USGS NAWQA
CONNECTICUT	1993-94	35	13	1	12	0.2	22	13	0	0	0	USGS NAWQA
ALBANY	1993-94	22	4	0	4	0.2	16	4	0	0	0	USGS NAWQA
LAS VEGAS	1993	33	4	1	3	0.2	29	3	1	0	0	USGS NAWQA
RENO-SPARKS	1994	28	6	1	4	0.2	22	4	0	1	1	USGS NAWQA
ALBUQUERQUE	1993	24	1	1	0	0.2	23	1	0	0	0	USGS NAWQA
DENVER	1993	29	23	6	17	0.2	6	19	0	2	2	USGS NAWQA
DALLAS-FORT WORTH	1993	17	3	0	4	0.2	14	4	0	0	0	USGS NAWQA
<b>TOTALS</b>		<b>211</b>	<b>56</b>	<b>11</b>	<b>45</b>	<b>-</b>	<b>155</b>	<b>50</b>	<b>1</b>	<b>3</b>	<b>1</b>	
<b>PERCENTS</b>		<b>100%</b>	<b>26.54%</b>	<b>5.21%</b>	<b>21.33%</b>	<b>-</b>	<b>73.46%</b>	<b>23.70%</b>	<b>0.47%</b>	<b>1.42%</b>	<b>1.42%</b>	

Explanation:

1 = local source identified by presence of benzene, toluene, xylene, ethylbenzene, and/or by TOC less than 2.0 ug/L

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TABLE 23 - SUMMARY OF MTBE OCCURRENCE FROM USGS NAWQA STUDY

Nationwide - Deeper Wells:

- Of the 413 deeper wells sampled, 4 wells (1.0%) had detectable concentrations of MTBE
- Range = 0.2 to 1.3  $\mu\text{g/L}$
- Median when detected = unknown, but roughly 0.5 to 0.6  $\mu\text{g/L}$
- Median of all wells = below detection limit of 0.2  $\mu\text{g/L}$

Nationwide - Shallow Wells:

- Of the 773 shallow wells and springs sampled, 63 wells (8.2%) had detectable concentrations of MTBE
- Range = 0.2 to 23,000  $\mu\text{g/L}$
- Median when detected = 0.6  $\mu\text{g/L}$
- Median of all wells = below detection limit of 0.2  $\mu\text{g/L}$
- all five drinking water wells were non-detect for MTBE<sup>15</sup>

Agricultural Wells:

- Of the 562 shallow monitoring wells sampled, 7 wells (1.2%) had detectable concentrations of MTBE
- none (0.0%) exceeded the lower limit of the possible USEPA MCL of 20  $\mu\text{g/L}$
- Range = 0.2 to 1.3  $\mu\text{g/L}$
- Median when detected = 0.5  $\mu\text{g/L}$
- Median of all wells = below detection limit of 0.2  $\mu\text{g/L}$

Urban Wells:

- Of the 211 shallow monitoring wells sampled, 56 wells (26.5%) had detectable concentrations of MTBE
- 6 of 211 wells (3%) exceeded the lower limit of the possible USEPA MCL of 20  $\mu\text{g/L}$
- 3 of 211 wells (1.5%) exceeded the upper limit of the possible USEPA MCL of 200  $\mu\text{g/L}$
- Range = 0.2 to 23,000  $\mu\text{g/L}$
- Median when detected = 0.6  $\mu\text{g/L}$
- Median of all wells = below detection limit of 0.2  $\mu\text{g/L}$

Denver Urban Wells:

- Of the 29 shallow monitoring wells sampled, 23 wells (79%) had detectable concentrations of MTBE
- 6 of 29 wells (20%) exceeded the lower limit of the possible USEPA MCL of 20  $\mu\text{g/L}$
- 2 of 29 wells (6.9%) exceeded the upper limit of the possible USEPA MCL of 200  $\mu\text{g/L}$
- Range = 0.2 to 23,000  $\mu\text{g/L}$
- Median when detected = 0.6  $\mu\text{g/L}$
- Median of all wells = below detection limit of 0.2  $\mu\text{g/L}$

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<sup>15</sup> As per verbal communications with John Zogorski of the USGS.

### Laboratory and Analytical Concerns

When it was announced via press releases that 27% of the 211 shallow urban wells and springs sampled nationwide had MTBE present, there was concern that some of these detections may be false positives. The first concern was that other components may have been mis-identified as MTBE. A second concern was that there may be laboratory induced cross-contamination of the samples. MTBE is often used as an extractant in pesticide analyses and this might have caused laboratory contamination of the samples, glassware or atmosphere. Thirdly, since the detection limit used (0.2 µg/L) was 2.5 to 5.0 times lower than commercial laboratories, perhaps some other factor was contributing to the occurrence of false positives.

As MTBE elutes in a gas chromatograph quite early, and as there are few co-eluting peaks, mis-identification of MTBE seemed unlikely. Also, because all samples were analyzed in the same laboratory, then if some false positives were recorded for MTBE, then they should have occurred throughout the dataset, and not be clustered just in urban wells or in Denver urban wells, as appeared to be the case if these MTBE detections were false positives.

Concerns about false positives were greatly reduced when data was received (Appendix F) that in 46 trip blanks, field blanks and equipment rinsate blanks, none detected any MTBE. In addition, 277 laboratory blanks were analyzed from 1993-1995 and none showed any MTBE present above the detection limit of 0.2 µg/L (48). Verbal information from USGS personnel indicates that VOC analyses and pesticide extractions were done in separate portions of the laboratory with separate air circulation systems. Therefore, laboratory-induced cross-contamination seems quite unlikely. At this time, there is no reason to believe any false positive MTBE values are contained in the USGS NAWQA data set.

### Nationwide - Deeper Wells

The USGS NAWQA study found that of 413 deeper monitoring wells sampled, 4 wells (1.0%) had MTBE detected (48). Conversely, 99% of the wells sampled had no MTBE detected, even at the very low detection limit of 0.2 µg/L. This shows that dissolved-phase MTBE is not common in deeper ground water. The highest detection of MTBE in these 413 deeper wells was 1.3 µg/L. This supports the discussions presented earlier that MTBE contamination should primarily stay in shallow aquifer zones, and that if it did happen to reach a deeper well, there are numerous factors that act to greatly reduce the concentrations. As stated by the USGS (48), because these samples are from deeper aquifers, these results may provide a better indication of the contaminants that presently exist in drinking water supplies. As a result, this data suggests that deeper water supply wells should usually have good inherent protection from any localized MTBE plumes.

### Nationwide - Shallow Wells

The USGS NAWQA study found that of 773 shallow monitoring wells sampled, 63 wells (8.2%) had MTBE detected (48). Conversely, 91.8% of the wells sampled had no MTBE detected, even at the very low detection limit of 0.2 µg/L. This shows that dissolved-phase MTBE is not ubiquitous in shallow ground water. When MTBE was present, the median concentration was 0.6 µg/L; this is far below the 20 to 200 µg/L range under consideration by the USEPA as a Maximum Contaminant Level (MCL) for drinking water consumption.



### Agricultural Wells

Nationwide, only seven wells (1.2%) of the 562 tested had detections of MTBE and all seven were 1.3 µg/L or less (Table 21). These results match expectations in that rural, agricultural areas have fewer USTs and use less RFG and oxyfuels. Therefore, MTBE should be found in the ground water infrequently. Based on MTBE concentrations and a complete lack of co-occurring BTEX compounds, apparently none of these seven wells are associated with a local blended gasoline plume. Since all MTBE values are below 2.0 µg/L, this suggests that these seven detections might be attributable to wet precipitation MTBE reaching the shallow ground water.

Since only 1.2% of the widely dispersed agricultural-area monitoring wells had detections of MTBE below 2.0 µg/L, it seems likely that wet precipitation of MTBE is not a common, or frequent phenomenon. The agricultural area around Denver (i.e. South Platte) had no detections of MTBE which suggests that MTBE dissolved into wet precipitation is not extensive even near high MTBE-use areas. A detailed study of the air basins over these 30 selected ground-water study areas would more directly address this issue as the study could attempt to relate rainfall patterns to areas of MTBE-blended gasoline use.

### Urban Wells

Of the 211 shallow urban wells and springs sampled, 155 (73.5%) had no MTBE detected at the 0.2 µg/L level. Nationwide, fifty-six (56) of these sampling locales (26.5%) detected MTBE. A detailed breakdown is as follows:

- 155 (73.5%) had: MTBE < 0.2 µg/L. (none detected)
- 41 (19.4%) had: 0.2 < MTBE < 2.0 µg/L
- 9 (4.3%) had: 2.0 < MTBE < 20.0 µg/L
- 3 (1.4%) had: 20.0 < MTBE < 200 µg/L
- 3 (1.4%) had: MTBE > 200 µg/L

The range of detections was quite broad ranging from 0.2 to 23,000 µg/L. Similar to agricultural wells, many of the detections (41 of the 56) were 1.3 µg/L or less. The other 15 urban wells detected higher MTBE concentrations, perhaps due to local UST releases.

### Denver Urban Wells

Of the eight urban study areas, the most frequent occurrence of MTBE was discovered in the Denver, Colorado urban area. Some 23 of the 29 wells sampled (79%) detected MTBE (Table 22). In 1988 Denver was one of the first urban areas to begin extensive use of oxygenated fuels, particularly MTBE<sup>16</sup>. While there was initially some concern about these findings, careful analysis of the Denver data shows:

- all six Denver wells with MTBE > 20.0 µg/L had co-occurrence of BTEX and/or dissolved oxygen levels less than 0.6 mg/L. These wells are very likely near local plumes of MTBE-blended gasoline.
- the highest detection of MTBE in Denver residential area wells (presumably away from point sources) was 1.4 µg/L. Note: this is nearly the same as the highest detected in the agricultural area wells and the highest detected in the deeper wells, as well as the mean of the predicted equilibrium concentration in wet precipitation.
- all Denver wells above 1.4 µg/L MTBE were in industrial or commercial areas

Within the Denver area, landuse obviously affects the concentration range and the highest detected MTBE values. This is expected as far fewer point source releases should be detected in residential areas than in industrial and commercial areas that are, or were, operating fuel handling facilities or are next to such facilities. Landuse designation data for the other seven urban study areas is not yet available from the USGS. Reportedly, on-site designations of landuse were made when USGS personnel collected the ground-water samples. This data is being compiled and collated by USGS and should be available in late 1995/early 1996. Unfortunately, this data has not yet been received or reviewed by these authors and so landuse designation for wells in the other seven urban study areas is unknown. Therefore, the applicability of this apparent correlation can not be stated with certainty for the other seven urban areas.

### Resampling of Denver Urban Wells

In August 1995, 14 of the 23 wells in the Denver urban study area that previously had MTBE were resampled by USEPA. The raw data is contained in Appendix F. When comparing the recent August 1995 data to the July 1993 data, it can be seen that:

- of the 8 residential wells sampled, all remained below 1.1 µg/L of MTBE with no BTEX detections. The MTBE concentrations increased slightly in four wells, decreased slightly in two wells, and remained the same in two wells.
- of the 2 commercial wells resampled, one had a slight MTBE increase (3.5 up to 3.7 µg/L), while the other had a large increase in MTBE (5.1 to 55.4 µg/L) along with a large BTEX increase (668 up to 15,140 µg/L).

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<sup>16</sup> In 1988 MTBE had approximately 90% of the Denver oxygenate market and it now has roughly 20%.

The five highest MTBE detections nationwide all had co-occurrence of BTEX compounds and/or DO levels less than 0.6 mg/L. It seems very likely that these high MTBE levels are attributable to local releases of MTBE-blended gasoline, probably from USTs. In addition, the three highest of these five are the only ones (of the 1,186 sampled) that exceeded the possible DRAFT USEPA MCL of 200 µg/L for MTBE.

There are 9 wells (4%) that fall in a middle range of having MTBE greater than 2.0 µg/L, but less than 20 µg/L. The co-occurrence of BTEX in 2 wells, and the average DO concentration for these wells of 0.68 mg/L, both strongly suggest that blended gasoline is a likely source for some of these 9 wells. Based on the MTBE levels, stormwater runoff may be the source for some of these detections.

The 38 urban wells that had MTBE detections at, or below, 1.4 µg/L had an average DO concentration of 2.46 mg/L. This is quite close to the 2.55 mg/L seen in the 136 wells that had no MTBE detected. It is interpreted that these MTBE detections are primarily attributable to MTBE in wet precipitation as it could produce MTBE concentrations of less than 2.0 µg/L while not reducing DO levels. A few of these low-level MTBE detections may actually be the first indicators of local gasoline releases. However, positive identification would require time-series sampling of these wells to detect MTBE increases, DO decreases and, eventually, perhaps BTEX appearances.

It appears that the USGS sampling has probably detected two sources of MTBE in the ground water:

- 1) sub 2.0 µg/L concentrations of MTBE due to MTBE in wet precipitation. These wells typically have no BTEX and average DO = 2.46 mg/L.
- 2) higher concentrations of MTBE due to local releases of blended gasoline. These wells usually have BTEX present and/or depressed levels of DO (average = 0.6 mg/L)

Stormwater runoff may also be present as a minor third MTBE source, although it is not possible to as clearly isolate which wells were impacted by this source as it is for the wet precipitation and blended fuel spills.

## Significance of USGS Findings

Based upon the above discussions, the authors conclude the following from the USGS NAWQA Phase 1 study regarding MTBE.

- the USGS well selection process is biased towards finding and sampling wells impacted with MTBE from local point sources, especially in the urban industrial and urban commercial landuse areas that accounted for the highest MTBE concentrations in the NAWQA study.
- wet precipitation under worst-case, highly conservative conditions might produce MTBE concentration in ground water at, or below, 2.0  $\mu\text{g/L}$ . This may account for the MTBE of less than 2.0  $\mu\text{g/L}$  in 19% of the shallow urban wells and springs, as well as in 1.2% of shallow agricultural wells. BTEX concentrations were typically ND while DO levels averaged 2.46 mg/L, which is very close to the 2.55 mg/L detected in wells with no MTBE present.
- local gasoline spills were detected as MTBE concentrations of more than 20.0  $\mu\text{g/L}$  in 3% of the shallow urban wells (i.e. 6 wells). BTEX compounds were typically present while DO levels averaged 0.49 mg/L. Both these indicate a local gasoline spill source likely accounts for the MTBE.
- based on the co-occurrence of BTEX compounds, two other urban wells with MTBE greater than 2.0  $\mu\text{g/L}$ , but less than 20  $\mu\text{g/L}$ , are also apparently attributable to a local gasoline spill.
- there are 7 urban wells and springs (3.3%) for which MTBE was greater than 2.0  $\mu\text{g/L}$ , but less than 20  $\mu\text{g/L}$ , and for which the MTBE source is unclear. However, the reduced DO concentrations (average = 0.68 mg/L) suggest that local gasoline releases are likely sources for some of these wells while stormwater runoff containing small amounts of blended gasoline may account for others.
- only 1 of the 413 deeper wells had MTBE present and the maximum detected was 1.3  $\mu\text{g/L}$ . This indicates MTBE contamination primarily stays in shallow aquifer zones, and that deeper water supply wells should usually have good inherent protection from localized MTBE plumes.
- two different sources of MTBE contamination were apparently detected: wet precipitation and local gasoline spills. There is no known mechanism (physical, chemical or biological) that can cause MTBE concentrations from wet precipitation to "build-up or accumulate" in the subsurface. No such mechanism is needed to reasonably explain the USGS data and a second sampling of selected Denver urban wells did not support the existence of any MTBE buildup.
- continued periodic sampling of these wells would provide time-series data on MTBE, BTEX and DO concentrations. This data would help resolve questions regarding contamination trends and sources, particularly for wells that have MTBE as the only gasoline component.
- the MTBE findings of the USGS study need to be reviewed with the understanding that the dataset mixes MTBE occurrences from two distinct sources (wet precipitation and local gasoline releases) as well as from several different landuses.

## REMIEDIATING SUBSURFACE MTBE SPILLS

*Subsurface remediation* is the process of removing an unwanted compound from the soil and ground water to reduce contaminant mass and concentrations. If MTBE is introduced to the subsurface by wet precipitation, there should be no need for health-based remediation as the concentrations in ground water must be less than 2 µg/L. However, if MTBE impacts the subsurface by a release of blended gasoline, then MTBE concentrations may be high enough to warrant remediation (Table 15).

Remediation can have various meanings depending upon whether the goal is to contain the contamination (ex. stop ground-water movement), reduce the concentrations, or completely restore the aquifer to original concentrations<sup>17</sup>. In this report, remediation is used to mean the containment and removal of ground water that is impacted with elevated concentrations of BTEX and/or MTBE.

Containment prevents dissolved-phase contaminants from moving further downgradient and impacting a larger portion of the aquifer. Removal will reduce contaminant concentrations (both MTBE and hydrocarbons) in the ground water and reduce contaminant mass in the subsurface. Together containment and removal can usually prevent the dissolved-phase contamination from reaching potential receptors like drinking-water wells or surface water bodies.

Containment and removal of dissolved-phase contaminants requires that ground water be pumped from the ground, treated and discharged. Such a "pump and treat" approach can be very effective at controlling and removing impacted ground water, but is not an efficient way to remediate the entire subsurface to pristine conditions<sup>18</sup>. Fortunately, dissolved-phase MTBE does not readily adsorb onto soil organic matter and so a pump and treat approach is more effective at removing MTBE than at removing aromatic hydrocarbons (i.e. more of the MTBE will be in the water than in the soil and thus is easier to remove). Bass and Sylvia (93) agree that pumping and treating removes MTBE from the ground water relatively quickly. They report that at one site where the pumping system influent initially had MTBE at 3,000 µg/L, the concentration was reduced over several years of pumping to 50 µg/L (93). MTBE that remains in the bulk gasoline absorbed into the soil pores can act as a long-term source of MTBE.

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<sup>17</sup> It is recognized that restoring aquifers to original conditions is quite difficult due to many biological, physical, and chemical factors all acting to prevent complete restoration.

<sup>18</sup> This is because the contamination that absorbs into the soil pores and adsorbs onto soil organic matter both act as long-term sources of ground-water contamination that are hard to eliminate. Ground-water remediation efforts are usually more effective if the soil contamination is addressed simultaneously.

## Containment Methods

Containing and removing contaminated ground-water plumes usually involves the following:

- a thorough site assessment
- access to the impacted area
- recovery wells (to access ground water)
- recovery pumps (to pump out ground water)
- power supply and power lines
- water discharge lines
- piping trenches
- water treatment equipment
- various valves, pumps, and controllers
- building/shed to house equipment
- a permitted method of water disposal (sanitary sewer, surface water body, reinjection, etc.)

If a spilled fuel does not contain MTBE as an octane enhancer, or as an RFG/oxyfuel additive, then the subsurface contamination will consist of BTEX, other aromatics, and non-aromatic hydrocarbons. Because benzene is a known carcinogen with a low Maximum Contaminant Level (MCL) of 5 µg/L, most subsurface gasoline remediation projects are driven by the need to contain and remediate benzene. If the benzene standard can be met, then the much higher MCLs (or action levels) for other compounds (like toluene, ethylbenzene and xylenes) are almost always met.

If the spilled gasoline does contain MTBE, then the dissolved-phase MTBE can be a separate driving force for the ground-water remediation. Because MTBE moves faster through the aquifer than the BTEX compounds, it is usually found on the downgradient "leading" edge of a gasoline plume. Additionally, approximately 1.5 to 2.0 times as much aquifer area will be impacted by MTBE than by BTEX.

### Horizontal Extent of MTBE Plumes to Be Contained

The MTBE plume in most aquifers may only be a mere 1.1 to 1.5 times larger than the BTEX plume if the time since the spill has been small (ex: less than one year); see Table G-1 of Reference 61 for an example. This is because initially the MTBE is only able to outdistance the BTEX due to the difference in their retardation factors. For example, in the low organic soils of the Borden aquifer, for aromatics the  $R_f = 1.1-1.5$ , while for MTBE the  $R_f = 1.00$  (61)<sup>19</sup>.

However, when the time since the fuel spill is great, the MTBE-only plume may have a much larger horizontal extent than the retardation difference alone could account for. This is because the natural biodegradation of the hydrocarbons (94) has caused them to reduce their concentrations and to migrate even further behind the MTBE (61). At the 30 blended gasoline spills reviewed by the author (Davidson), it had been two to seven years since the fuel release. When considered two-dimensionally,

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<sup>19</sup> If the aquifer has very high soil organic matter, then BTEX retardation factors might be 2 to 4. Meanwhile, the MTBE retardation may still only be nearly 1.00. This great retardation might cause the MTBE plume to extend several times further downgradient than the BTEX plume. However, this situation is atypical and could be readily identified by the high  $F_{oc}$  in the soil.

the area contaminated by MTBE was 1.5 to 2.0 times larger than the area impacted by BTEX alone (Figure 5).

As time progresses, this biodegradation difference will cause the MTBE to pull further away from the aromatics and increase the distance traveled ratios. If the time since the spill has been on the scale of five to ten years, the MTBE-only plume might extend more than twice as far downgradient than the BTEX plume. However, since MTBE use in gasoline was not wide-spread prior to the late 1980s, few gasoline releases have had enough time to create such large distances between the MTBE plume and the BTEX plume due to biodegradation-rate differences. Therefore, a reasonable assumption is that MTBE plumes are typically 2.0 times larger than the BTEX plume.

#### Water Treatment Methods

Detailed studies show that after pumping out ground water impacted with MTBE, the MTBE can be successfully removed from the water by a variety of techniques (44, 87). Almost any technique that removes BTEX from water can remove MTBE. However, due to its lower volatility, lower adsorption to granulated activated carbon, and poor biodegradability, removing MTBE from water is almost always more expensive than removing BTEX components.

The most cost-effective techniques are air stripping, or air stripping followed by a carbon adsorption system to remove the remaining traces of MTBE. These two techniques are used in most projects that remediate ground water impacted by BTEX and MTBE (1, 43, 55, 61).

Field experience has shown that air stripping is quite reliable. It can remove up to 99% of the MTBE from ground water, provided the stripping system is large enough, carefully designed, and properly operated (43). MTBE is harder to remove by air stripping than BTEX components because of its low Henry's Law Constant (i.e. lower volatility from water) which often mandates high air flows for effective air stripping (93). Alternately, multiple air strippers in a series may be required. It is common to see air stripping removal rates for benzene of 80% to 99%, while MTBE removal rates are often only 50% to 90% (43). MTBE can be more readily air stripped if the water is heated prior to stripping (49, 93) but this can significantly increase treatment costs (44).

The drawback to air stripping is that the off-gas will release the MTBE and BTEX components to the atmosphere. Such air discharges are undesirable in many areas, and not permissible in many air quality non-attainment areas unless some form of off-gas treatment is used. Off-gas treatment can be done by incineration, catalytic conversion, or vapor-phase carbon adsorption to capture the contaminants. However, these technologies can increase total treatment cost by about 75% (44).

Off-gas emissions can be avoided by using above-ground biological treaters, UV/ozone systems, or carbon adsorption systems to remediate the ground water (1, 43, 44). However, each of these technologies are much more expensive than air stripping or air stripping with a subsequent carbon adsorption system.

### Cost of Remediating MTBE Plumes

There are numerous factors that make remediating the MTBE portion of subsurface hydrocarbon plumes more difficult and costly than remediating just the BTEX. Specifically:

- the MTBE plume is often 1.5 to 2.0 times as big as the BTEX plume
- the greater areal extent of the MTBE plume requires a more extensive assessment
- the greater areal extent of the MTBE plume requires more complex and costly access issues so that assessment and remediation can be conducted
- the greater areal extent of the MTBE plume requires more recovery wells, pumps, and lines
- a larger ground-water discharge rate will be needed to control this larger plume, which increases capital equipment costs, installation costs, and operating costs
- larger and/or more air strippers are needed to account for MTBE's lower volatility than BTEX; this increases both capital equipment costs and power costs

It is useful to determine how much more expensive it is to remediate dissolved-phase plumes of BTEX and MTBE as compared to just remediating the BTEX portions of plumes. To do this, several assumptions must be made so the costs can be compared. Appendix G details the assumptions and calculations made in this report to determine how much more it costs to remediate MTBE plumes. Based on field experience and the literature, the remedial design characteristics for a typical UST release site were as follows:

#### Remediate Just BTEX Plume:

- assessment completed
- 2 recovery wells with pumps used to remove ground water
- a total of 10 gpm must be pumped to contain plume
- BTEX treatment by air stripper
- BTEX influent ranges from 5,000 - 20,000  $\mu\text{g/L}$
- no off-gas treatment/control required
- treated water discharged by permit into sanitary or storm sewer

#### Remediate MTBE and BTEX Plumes:

- assessment completed
- MTBE plume covers an area twice as large as the BTEX plume
- 4 recovery wells with pumps used to remove ground water (two BTEX/MTBE removal wells closer to source, and two MTBE-only removal wells further downgradient)
- a total of 20 gpm must be pumped to contain total plume (10 gpm for BTEX/MTBE plume, 10 gpm for MTBE-only plume)
- BTEX and MTBE treatment by air stripper
- BTEX influent ranges from 5,000 - 20,000  $\mu\text{g/L}$
- MTBE influent is 2,000 - 10,000  $\mu\text{g/L}$
- no off-gas treatment/control required
- treated water discharged by permit into sanitary or storm sewer



Based on a review of the literature, and upon the author's experience, this BTEX removal system is considered a "typical" UST ground-water pump and treat operation. The second system described is for removing both the BTEX and MTBE plumes. It represents what is needed to control a "typical" BTEX, MTBE plume, based on the literature and the author's experience (see Appendix G).

### Cost Comparisons

General cost estimates are used for typical BTEX and BTEX/MTBE plumes in these comparisons. As a result, the cost comparisons here are not appropriate for any individual site, but are considered to be reasonable for a typical blended gasoline release.

As described in Appendix G, the cost for a pump and treat system for an average BTEX plume resulting from a UST release was obtained from the literature (95). The total capital, installation and operation costs cited for such a system ranged from \$250,000 to \$300,000 for 3 to 10 years of operation (95). The mean would be \$275,000 for a typical system to operate 6.5 years.

As described in Appendix G, two independent approaches were used to determine costs for controlling a typical MTBE plume (in addition to the BTEX portion of the plume). The first approach considered the additional elements needed to remediate the MTBE portion of a typical MTBE-blended gasoline plume. It qualitatively estimated that this would require 2 to 3 times the expenditures as just controlling the BTEX portion of the plume.

The second approach calculated the cost increase by using per/day cost estimates for remediating BTEX and MTBE impacted ground water (44). As detailed in Appendix G, this second approach indicated that remediating the expansive MTBE portion of a typical gasoline spill plume, along with the smaller BTEX plume, would require \$725,000 to \$861,000 for 6.5 years of operation. Table 24 shows the calculations which indicate that adding containment and treatment of the more far-reaching, MTBE-only portion of the blended gasoline plume can increase ground-water remediation costs by a factor of 2.6 to 3.1. The qualitative and quantitative approaches both converged on essentially this same cost factor range.

TABLE 24  
MTBE REMEDIATION COSTS

Treatment Technique	Total Treatment Costs			Cost Ratio Compared to BTEX only of \$275,000
	\$/day	operating days <sup>2</sup>	\$ for 6.5 years	
Air Stripping	309	2,347	725,223	2.64
Air Stripping with Aqueous Phase Carbon Adsorption	367	2,347	861,349	3.13

Notes:

1. Includes installation, capital equipment, operation, maintenance
2. Assumes 361 days per year as one day each quarter needed for maintenance. Therefore, 361 days per year x 6.5 years = 2346.5, round to 2347 days

While this general estimate is not necessarily accurate for any particular spill, it demonstrates that remediating the ground water from the downgradient MTBE portion of a blended fuel spill can increase remediation costs by several times. If regulations required remediation of MTBE-impacted ground water, then this additional expense could be mandated at many of the UST leaks in regions using MTBE-blended gasoline.

In a general sense, the appropriateness of such remediation requirements must be weighed against the trends in UST releases, MTBE mass losses to the subsurface, and population exposed. For any specific site, the appropriateness of remediation should be determined based upon size and concentration of both the BTEX and MTBE plumes, natural attenuation, MTBE concentration reductions by dispersion and volatilization, potential receptors, risk of exposure to contamination, and possible corrective actions (84).

## SUMMARY AND CONCLUSIONS

In this report, calculations have been made and data presented regarding many aspects of MTBE occurrence in ground water and drinking water. Major conclusions are:

- the causes, trends, patterns, and typical concentrations of MTBE-impacted ground water are well understood. While additional studies and ground-water analyses would enhance the database, the MTBE results from more than 5,350 wells and springs<sup>29</sup> from across the country that were summarized and analyzed in this report establish the scope of the problem and the major processes involved.
- the vast majority of MTBE releases go into the atmosphere where oxidation processes act to break it down.
- releases of MTBE into the subsurface should decrease substantially in the next five years due to MTBE use patterns and due to improving leak prevention and detection for USTs (which are a major source of MTBE releases to the subsurface).
- MTBE from blended gasoline spills dissolved into ground water does not cause co-solvency of hydrocarbons. In fact, the presence of MTBE lowers BTEX concentrations in ground water.
- the presence of MTBE does not apparently inhibit biodegradation of aromatic hydrocarbons.
- the MTBE portion of a blended gasoline plume is typically 1.5 to 2.0 times larger than the BTEX portion.
- MTBE in ground water comes primarily from two sources: wet precipitation and local releases of MTBE-blended gasoline.
- equilibrium calculations indicate that MTBE can only dissolve into wet precipitation at concentrations less than 2 µg/L. Therefore, MTBE dissolved into wet precipitation can only create concentrations in ground water greater equal to, or less than 2 µg/L.
- most wells located away from point sources of MTBE-blended gasoline found contained no detectable MTBE (i.e. 99% of USGS deeper wells, 99% of USGS agricultural wells, all residential wells in Denver, more than 97% of public water supply wells, more than 94% of private water supply wells). Those wells away from point sources that did contain MTBE had concentrations less than 1.4 µg/L, which is very close to the 1.2 µg/L predicted annual mean MTBE concentration in wet precipitation.
- the USGS NAWQA study detected MTBE in shallow ground water at a median concentration less than the 0.2 µg/L detection limit. In those wells that did have MTBE, the median concentration detected was 0.6 µg/L.

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<sup>29</sup> 5,350 = Total number of wells as summarized in Table 15 (353 monitoring wells), Table 18 (2,499 public wells), Table 19 (1,291 private wells), USGS NAWQA (211 + 562 + 413 = 1,186 wells and springs), plus several dozen more wells from the various studies referenced throughout the paper.

- MTBE concentrations in ground water due to blended gasoline spills are 1 to 5 orders of magnitude higher those due to wet precipitation.
- local, point-source MTBE-blended gasoline releases can create MTBE concentrations in ground water above health standards for drinking water consumption. In rare cases, pure MTBE or MTBE-impacted tank bottom waters may also create higher MTBE concentrations in ground water.
- about 0.04% of public water supply wells and 0.3% of private water supply wells may have MTBE at concentrations higher than 200 µg/L. Factors like spatial separation, geologic separation, blending, volatilization, and others all help prevent impact by, and reduce concentrations of MTBE in water supply wells. Low odor and taste detection thresholds help prevent water consumption from impacted wells.
- remediating subsurface MTBE ground-water contamination can be conducted using existing technologies, but costs about 2.6 to 3.1 times as much as remediating the BTEX components.

#### **General Qualifying Statement**

In preparing this report, actual measured values were used whenever possible and references provided. However, some baseline values needed in the calculations were not available in the literature or through applicable organizations (i.e. USEPA, API, PMAA, PEI, etc.). In such cases, preliminary estimates were made based upon the available data, literature citations, reasonable extrapolations, and the authors' experience. The authors welcome receipt of additional references and values to further refine these estimates.