ACS SYMPOSIUM SERIES **799**

Oxygenates in Gasoline

Environmental Aspects

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Oxygenates in gasoline : environmental aspects

Foreword

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Preface

At the writing of this book the issue of methyl *tert*-butyl ether (MTBE) use in gasoline has taken center stage with the U.S. Environmental Protection Agency's (EPA) announcement that it will use the Toxic Substances Control Act (TSCA) to reduce or eliminate MTBE in gasoline by approximately 2003. Further, the U.S. EPA and the Department of Agriculture have called on Congress to pass legislation requiring that MTBE be replaced with a renewable fuel such as ethanol, proposing that we have a renewable fuel standard rather than an oxygen mandate. Adding further concerns to the MTBE debate is the National Academy of Sciences study, which concluded that the addition of oxygenated compounds to gasoline formulations does little to reduce smog levels. A further wrinkle in the U.S. MTBE ban is the lawsuits filed under the North American Free Trade Agreement (NAFTA). Methanex Corporation of Canada, the world's largest methanol producer sells methanol to MTBE producers. Methanex filed a complaint in December 1999, under NAFTA, claiming that the announcement of California's MTBE ban cost them $1 billion in share value. The NAFTA provision currently being cited by Methanex is the same provision Ethyl Corporation used when Canada tried to ban the gasoline octane methylcyclopentadienyl manganese tricarbonyl (MMT). The Canadian government lost this suit, had to pay monetary compensation, and the MMT ban was overturned, indicating that NAFTA suits could override domestic environmental policies. Therefore, it appears that the issues surrounding MTBE use are not likely to be resolved anytime soon.

California opposes requirements to add any oxygenates, including ethanol to gasoline. The California Air Resources Board has requested that the EPA waive the section of the Clean Air Act that requires that addition of compounds like MTBE and ethanol citing advances in refining techniques that can make a reformulated gasoline meeting air quality standards without adding any oxygenates. In March 1999, California Governor Gray Davis signed an Executive Order phasing out the use of MTBE in California gasoline by the end of 2002. Of concern to many Californians, who pay among the highest gasoline prices in the United States, is the California Energy Commission's report (Staff

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Findings: Timetable for the Phaseout of MTBE from California's Gasoline Supply, P300–99–003. Staff Findings, June 1999), which estimated that a requirement for the addition of ethanol could add 6 cents/gallon to the price of gasoline. This is in part because California does not have large-scale ethanol production facilities and ethanol would need to be trucked in from the Midwest. It is estimated that a switch to ethanol would require a doubling of current ethanol production levels to 3.6 billion gallons/year with one-third of that needed to meet California's supply requirements.

Regardless of whether MTBE is banned today, as a society we will be faced with environmental contamination from MTBE for an extended period due to MTBE's physical properties. MTBE is highly soluble and very mobile in water. It does not tend to sorb to aquifer materials thereby migrating long distances in the subsurface environment. It resists biodegradation due to its chemical structure, degrading very slowly in groundwater. At very low levels, MTBE imparts an unpleasant taste and odor to drinking water. A study by Johnson, Pankow, Zogorski, et al. (Johnson, R. L. et al. *Environ. Sci. Technol.,* May 1, 2000, 210A–217A) concluded that as many as 9000 community water supply wells in 31 states may be contaminated with MTBE and estimated that MTBE releases may continue to reveal themselves as problematic sources of groundwater contamination in the United states until at least 2010.

The chapters presented in this book present a discussion of the latest information on the issues surrounding the presence of fuel oxygenates in the environment.

We are particularly pleased with the American Chemical Society's (ACS) interest in publishing a book on the subject of the environmental aspects of oxygenates in gasoline. We greatly appreciate their support in promoting this subject to chemists and technical personnel in other fields of study. The editors express their sincerest gratitude to the authors for careful preparation of their chapters, to the reviewers of the chapters who graciously volunteered their time and expertise and to Anne Wilson and Kelly Dennis of the ACS Books Department for their encouragement, assistance, and patience.

This book was edited by Arthur F. Diaz and Donna L Drogos in their private capacities. No official support or endorsement of or from the University or the Santa Clara Valley Water District is intended or should be inferred.

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Chapter 1

Methyl *tert*-Butyl Ether in Ground and Surface Water of the United States

National-Scale Relations between MTBE Occurrence in Surface and Ground Water and MTBE Use in Gasoline

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The detection frequency of methyl *tert*-butyl ether (MTBE) in ground and surface water of the United States is positively related to the content of MTBE in gasoline in various metropolitan areas of the U.S. The frequency of detection of MTBE is generally higher in areas that use larger amounts of MTBE in gasoline. Sampling of surface and ground water by the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program between 1993 and 1998 revealed a frequent detection of low concentrations of MTBE. In this analysis, data from several national-scale gasoline surveys are examined and data from one survey that is most extensive in geographic and temporal coverage is used to relate the detection of MTBE in ground and surface water to the volumetric content of MTBE in gasoline.

Introduction

Oxygenates are compounds that contain oxygen. These compounds are commonly used today in the United States to add oxygen to gasoline as an octane enhancer and for more complete combustion of gasoline. Octane enhancement began in the late 1970's with the phase-out of tetraethyl lead from gasoline. The use of oxygenates was expanded as a result of the enactment of the Clean Air Act (CAA) Amendments of 1990. The CAA Amendments mandate that oxygen must be added to gasoline in areas that do not meet National Ambient Air Quality Standards (NAAQS) for carbon monoxide and ozone (*1*).

Two primary areas of oxygenate use in fuel were specified by the CAA Amendments: 1) the Oxygenated Fuels Program (OXY) in which gasoline must contain 2.7% oxygen by weight during the cold season in areas that fail to meet NAAQS for carbon monoxide, and 2) the Reformulated Gasoline Program (RFG) in which gasoline must contain 2% oxygen by weight year-round in areas having the highest levels of tropospheric ozone (*1*).

Although the CAA Amendments do not specify which oxygenate must be added to gasoline, the one used most commonly is methyl *tert*-butyl ether (MTBE). MTBE has been detected frequently in ground and surface water in areas that use it as a fuel oxygenate, causing concern about water quality in these areas. Understanding the relations between MTBE occurrence and its usage is important for determining if regulations meant to improve the Nation's air quality have resulted in degradation of water quality and inadvertent, detrimental effects.

MTBE Use and Environmental Occurrence

To meet the oxygen requirements of the CAA Amendments, gasoline in designated OXY areas must contain 15% MTBE by volume to achieve 2.7% oxygen by weight and gasoline in designated RFG areas must contain 11% MTBE by volume to achieve 2% oxygen by weight. Some areas of the country that meet NAAQS have chosen to voluntarily use RFG gasoline. Because of its widespread usage, MTBE is manufactured in great quantities with almost 12 billion liters produced in the U.S. in 1998 (*2*). In addition, large quantities of MTBE are also imported annually. Although MTBE is the most commonly used oxygenate in areas of NAAQS non-attainment, it is not used in all areas. Ethanol is the second most commonly used fuel oxygenate. In 1998, 5.3 billion liters of ethanol were produced. Other alkyl ether oxygenates are used to achieve the oxygen requirements of the CAA Amendments including *tert*-amyl

methyl ether (TAME), diisopropyl ether (DIPE), and ethyl *tert*-butyl ether (ETBE). These other ethers are used much less for fuel oxygenation than MTBE.

The combination of the large-scale production and use of MTBE combined with its high solubility, low soil adsorption, and low biodegradability, has resulted in its detection in many ground- and surface-water systems. Sampling of ground water at a national scale by the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program between 1993 and 1998 indicated a frequent detection of low concentrations of MTBE (*3*). The samples were obtained from a variety of confined and unconfined aquifers and from wells with a variety of water uses. Also, some samples are from studies of ground-water quality in specific land use areas such as urban and agricultural whereas others represent broad assessments of regional aquifers.

MTBE also has been detected in surface water sampled by the USGS (*4*). In general, the USGS surface-water samples were collected in small, perennial streams in urban areas that do not receive large wastewater effluent discharges. In samples taken from 14 urban areas between 1996 and 1998, about 39% contained detectable concentrations of MTBE (minimum reporting concentration varied from 0.1 to 1.0 µg/L). In another analysis, at least one sample from 10 of the 12 urban areas had a detectable concentration of MTBE (*5*).

MTBE also has been detected in drinking water in some areas of the country. Of 1,190 community water systems sampled in 10 northeastern states, MTBE was detected in one or more samples in about 7% of the systems at a minimum reporting concentration of 1.0 µg/L (*6*). MTBE was detected in about 7% of systems that are supplied exclusively by ground water and about 6% of the systems that are supplied exclusively by surface water.

For ground water, detection of MTBE appears to be related to its usage patterns in gasoline. In ground water, MTBE was detected in about 21% of samples in areas that use substantial (> 5% by volume in gasoline) amounts of MTBE (generally either RFG or OXY areas) and about 2% of samples in areas that do not use substantial (≤ 5% by volume in gasoline) amounts of MTBE (*3*). The minimum concentration used to compute frequency of detection in this analysis was 0.2 µg/L. The frequency of occurrence of MTBE in drinking water is also related to the usage patterns of MTBE in gasoline (*6*).

As in ground water, the occurrence of MTBE in surface water is related to the use of MTBE in gasoline. At least 76% of the samples in which MTBE was detected were collected from within a designated RFG or OXY area (*5*). MTBE also has been detected in urban storm water with about 7% of samples collected by the USGS between 1991 and 1995 containing detectable concentrations of MTBE (minimum reporting concentrations of 0.2 or 1.0 µg/L). As with other

data from ground water and surface water, MTBE detection in urban stormwater was related to usage patterns of the compound (*4*).

Gasoline Surveys

Usage of MTBE can be described in several ways. In general, most RFG areas use MTBE, whereas most OXY areas use ethanol. Knowing that an area is designated as RFG or OXY can give some insight into the type of oxygenate being used, but this information alone cannot specifically determine which oxygenate is used in specific metropolitan areas and in what amounts. For example, some areas use ethanol exclusively as a fuel oxygenate. Data on the volumes of oxygenates and other compounds in gasoline are available from several sources collectively referred to here as gasoline surveys. The gasoline surveys provide the most definitive knowledge of which oxygenate, if any, and what volumes of that oxygenate are being used in various areas of the United States. This information is important in water-quality assessments for relating the detection of MTBE in water to patterns of usage of MTBE in gasoline.

Table 1 summarizes general information on three surveys that have been conducted by 1) the National Institute for Petroleum and Energy Research (NIPER), 2) the Motor Vehicle Manufacturers Association (MVMA), and 3) the U.S. Environmental Protection Agency (USEPA). In general, the surveys collected data on samples of various grades and blends of gasoline from selected cities throughout the United States. The samples were tested for physical properties and constituents including octane number, specific gravity, and volumes of olefins, aromatics, benzene, alcohols, and various ether oxygenates. The purpose of the NIPER survey is generally to provide comparative information to interested companies on the physical and chemical properties of fuels. The purpose of the USEPA survey is to verify that oxygen content in gasoline is sufficient to meet the USEPA RFG program requirements.

The data in each survey has its own utility based on the type of assessment that is undertaken. The NIPER survey contains data for the greatest number of cities and samples analyzed. In addition, the raw NIPER data are available in computer files that facilitate analyses of the relations between the occurrence of MTBE in surface or ground water and the use of MTBE in gasoline. Data on the proportion of oxygenates in gasoline were initially reported by the NIPER survey for 1990-1991, and data on the proportions of individual ether oxygenates in gasoline have been reported since the summer of 1993. The data on total ether oxygenates reported by NIPER for the period 1990-1993 is assumed here to represent MTBE. Data from the MVMA survey can help to fill in gaps in the NIPER data and to extend information on oxygenate use prior to

Table I. General Characteristics of Gasoline Surveys

Name of survey	Agency conducting survey	Geographic coverage	Time span of analysis for MTBE and other oxygenates	Number of samples	Participation
National Institute for Petroleum and Energy Research (NIPER) survey	U.S Department of Energy	An average of 66 cities throughout the U.S. each year	1990-1999	Thousands each year	Voluntary by companies interested in fuel comparisons
Motor Vehicle Manufacturers Association (MVMA) National gasoline survey	Motor Vehicle Manufacturers Association	23 cities throughout the U.S.	Summer of 1988 to winter of 1994-1995	Hundreds each year	Unknown
USEPA RFG survey	Reformulated Gasoline Survey Association for the U.S. Environmental Protection Agency	23 metropolitan areas throughout the U.S.	1995-1999	Thousands each year	Voluntary by members of the Reformulated Gasoline Survey Association, a group of refiners, importers, and blenders of gasoline

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1990. Also, because many of the cities sampled for the MVMA survey overlap with cities sampled for the NIPER survey, it is possible to make comparisons of data from the two surveys and evaluate variability in the amounts of oxygenates used in a metropolitan area. The USEPA RFG survey provides data on the proportion of oxygenates used in gasoline in RFG areas.

The USEPA also collects information on the proportion of oxygenates in gasoline in OXY areas. USEPA regional offices, through contacts within individual state energy offices, compile this information from state officials who are familiar with the proportions of oxygenates used in gasoline within their states via surveys of local refiners, blenders, importers, and distributors of gasoline. This information is compiled for each metropolitan area required to use oxygenated fuels in the winter for the OXY program.

The NIPER data on MTBE content (as percent by volume) in gasoline is the most useful for water quality analyses since it samples the largest number of cities, has the greatest available temporal extent of data on MTBE in gasoline, and is ongoing. Consequently, the NIPER data provides the clearest picture of MTBE and ethanol usage in selected urban areas for the last ten years.

Current National Distribution of MTBE and Ethanol Use

Figure 1 shows areas of the conterminous United States currently (summer 2000) designated by the USEPA as RFG and also shows metropolitan areas where MTBE comprised 9-13% of gasoline by volume. The volume of MTBE in gasoline for areas shown in figure 1 was determined from the NIPER survey for the period of the winter of 1998 through the summer of 1999 by taking a median of all sample values for that period for each metropolitan area. This is the most currently available data from the NIPER survey. The areas designated as RFG include both mandatory and voluntary participation in the program. Metropolitan areas with low MTBE use (0-3%) are believed to be using MTBE primarily for octane enhancement and are not shown in this figure.

Figure 2 shows areas of the conterminous United States currently (summer 2000) designated by the USPEA as OXY and also metropolitan areas where ethanol comprised 8-11% of gasoline by volume. The volume of ethanol in gasoline for areas shown in figure 2 was determined from the NIPER survey for the period of the winter of 1998 through the summer of 1999 by taking a median of all sample values for that period for each metropolitan area. This is the most currently available data from the NIPER survey. Metropolitan areas with low ethanol use (0-1%) are believed to be using ethanol primarily for octane enhancement and are not shown in this figure. Some areas are designated as both RFG and OXY. Since these federally-mandated oxygenate-use areas overlap they are shown as simply RFG areas in Figure 1.

Figure 1. Areas currently designated as RFG and metropolitan areas where MTBE content in gasoline is 9 to 13% by volume.
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Figure 2. Areas currently designated as OXY and metropolitan areas where ethanol content in gasoline is 8 to 11% by volume.
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Metropolitan areas shown in figures 1 and 2 are delineated by the boundaries of U.S. Bureau of the Census Consolidated Metropolitan Statistical Areas and Metropolitan Statistical Areas in combination with data on population density identifying urban areas. RFG and OXY areas are displayed as counties within metropolitan areas that have been identified by USEPA as participating in these programs. In some instances only portions of a county are within a program area; however, these boundaries are not available and the full county is shown. For these reasons, metropolitan areas shown on these figures do not overlap exactly with RFG and OXY areas.

There is generally good agreement between the areas designated as RFG and metropolitan areas that have high MTBE use (9-13% by volume) in gasoline (fig. 1). However, some cities in RFG areas, for example Chicago, IL, use another fuel oxygenate such as ethanol (fig. 2). Other cities or areas have voluntarily entered (opted in) or removed (opted out) themselves from the RFG program or have been redesignated into or out of the program. For example, Phoenix, AZ, voluntarily entered the RFG program in 1997 and opted out in June 1998. Areas of southern Maine voluntarily entered the RFG program and opted out in 1999. There is also generally good agreement between the areas designated as OXY and the metropolitan areas that have high ethanol use (8-11% by volume). This confirms the general assumption that OXY areas primarily use ethanol to provide oxygen in gasoline.

The use of ethanol in many OXY areas is confirmed by information compiled by the USEPA. The following cities are in OXY areas and use only ethanol to achieve oxygen requirements: Minneapolis, MN, Las Vegas, NV, El Paso, TX, and Spokane, WA. Some cities in the OXY program are using a combination of ethanol and MTBE and/or TAME to meet oxygen requirements. One example is Denver, CO that, in the winter of 1998-1999, used a mixture of ethanol, TAME and MTBE to meet oxygen requirements.

An example of the utility of gasoline survey data to water-quality assessments is analyses of ground-water data from the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. Using NAWQA data, the percent occurrence of MTBE in ground water in metropolitan areas that use substantial amounts of MTBE (> 5% by volume) was about 21%, compared to about 2% in areas that do not use substantial amounts of MTBE (≤ 5% by volume) (3). When several other factors are considered in a logistic regression model including MTBE usage in RFG or OXY gasoline areas (≥ 3% by volume) as a factor, a 4-6 fold increase in the detection frequency of MTBE in ground water is found when compared to areas that do not use MTBE or use it only for octane enhancement (< 3% by volume).

Overall, the usage pattern of fuel oxygenates, and especially of MTBE, across the country is complex and changes with time. Although the gasoline

survey data are useful in distinguishing amounts of MTBE in gasoline between various urban areas, they are applicable only to metropolitan areas at the present time. In water-quality assessments, areas outside of metropolitan areas are simply assigned as having low or unknown MTBE use. However, locations that are close to, but not within, an urban area that is designated as RFG or OXY may be using gasoline containing a high percentage of MTBE if they receive the same gasoline blend as the nearby city. In addition, the extent of the metropolitan boundaries used for the gasoline surveys is not clear in many cases. If the boundaries of cities, as defined by gasoline surveys, were more clearly delineated and if a random sampling of smaller cities also were included, the data in these surveys would have much greater value to water-quality assessments.

Relations Between MTBE Environmental Occurrence and Use in Gasoline

Using NIPER data, areas of the country where NAWQA has sampled surface and ground water were classified into two MTBE use categories: 1) high MTBE use and 2) low/no/unknown MTBE use. High MTBE use areas were defined as areas where MTBE content in gasoline was an average of > 2% (> 6% for seasonal use only) by volume whereas low/no/unknown MTBE use areas were defined as areas where MTBE content in gasoline was an average of ≤ 2% by volume or was unknown. Areas where MTBE content in gasoline was an average of ≤ 2% by volume may be using MTBE for octane enhancement only. The MTBE content in gasoline represents a long-term arithmetic mean for the period of record prior to the water sampling date. The value of 2% was chosen because it represents a break point between distinct groups of generally high and low values. The value of 2% is a lower cut-off point than previous analyses (3) because a longer time period was considered for the averages which resulted in lower values for all metropolitan areas.

These two MTBE use areas can then also be arranged into RFG, OXY or other (no NAAQS nonattainments) areas based on air-quality requirements. Areas that are designated as both RFG and OXY have been placed into the RFG category. By comparing detection frequencies between MTBE use categories within each air-quality requirement area, it is possible to gain insight into the relation between the detection of MTBE and its use.

Figures 3 and 4 illustrate the differences in percent detection of MTBE in ground and surface water for both MTBE use categories within each federally-mandated oxygenate use area. For ground and surface water, the detection frequency of MTBE has been censored at a minimum concentration of 0.2 µg/L to allow for comparison of data with varying laboratory reporting levels.

The use of MTBE, as opposed to another oxygenate, in RFG and other areas generally results in a significant increase in the detection frequency of MTBE in ground water (fig. 3). In fact, the high use of MTBE in RFG areas results in an increase in the detection frequency of MTBE of 2 times and in OXY areas results in a 5 times increase in the detection frequency of MTBE (fig. 3). In other areas the high use of MTBE results in an increase in the detection frequency of MTBE of 3 times.

For surface water, the use of MTBE in RFG results in only a slight increase in the detection frequency of MTBE in RFG areas. It is unclear why the detection frequency of MTBE in areas where MTBE use is high is not substantially different from areas where MTBE use is low but it may be that many of the surface water systems sampled are dominated by ground water inflow and MTBE may be present in the ground water in these areas. There were no samples available in OXY areas with high MTBE use. For areas other than RFG or OXY, the frequency of detection of MTBE in surface water is lower for areas that use MTBE compared to areas where either no MTBE is used or its use is unknown. This apparent anomaly may be, in part, the result of the uncertainty involved in assigning an MTBE-use category to relatively large geographic areas such as surface- water drainage basins that may cross MTBE-use boundaries.

A more detailed analysis of the relations between the content of MTBE in gasoline and the detection frequency of MTBE in ground and surface water can be performed by using the percent by volume of MTBE in gasoline provided by NIPER. Frequencies of detection of MTBE were compared to percent volumes of MTBE in gasoline for selected metropolitan areas where NAWQA sampled surface and ground water and gasoline survey data were available (figs. 5 and 6). For ground water, 22 metropolitan areas had information on detection frequency and percent volume of MTBE in gasoline, whereas for surface water 10 metropolitan areas had this information. Each data point on Figures 5 and 6 represents a different metropolitan area. Table 2 lists the metropolitan areas represented in Figures 5 and 6.

The frequencies of detection of MTBE in Figures 5 and 6 were computed using a minimum reporting concentration for MTBE of 0.2 µg/L. For each metropolitan area, the frequencies of detection of MTBE were used in this analysis only if at least 10 samples were analyzed for MTBE. The percent volume of MTBE in gasoline shown in these figures was obtained for each metropolitan area by computing a long-term arithmetic mean of MTBE content (percent by volume) for all gasoline samples prior to the latest year of water sampling. If a metropolitan area had information on frequency of detection of
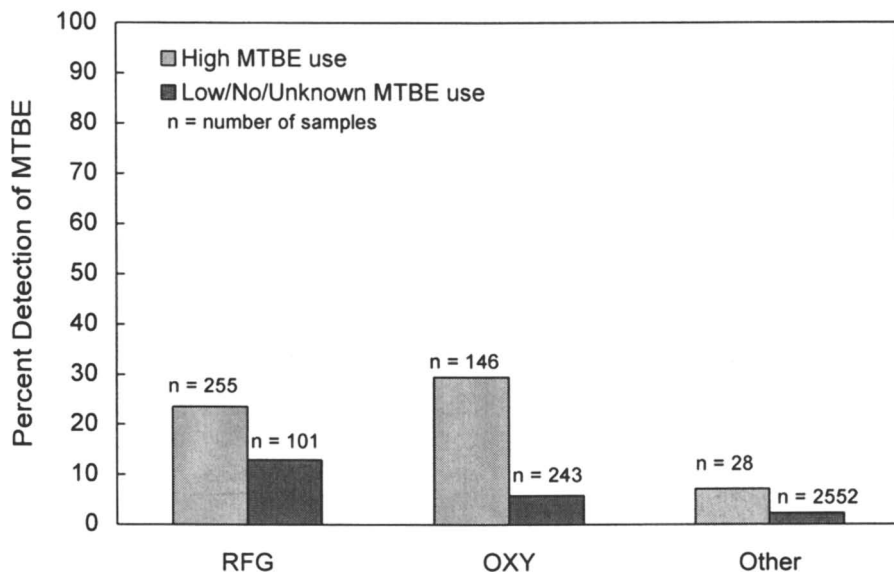
Figure 3. Frequency of detection of MTBE in samples of ground water (1993-2000) by MTBE use category (minimum concentration of 0.2μg/L).
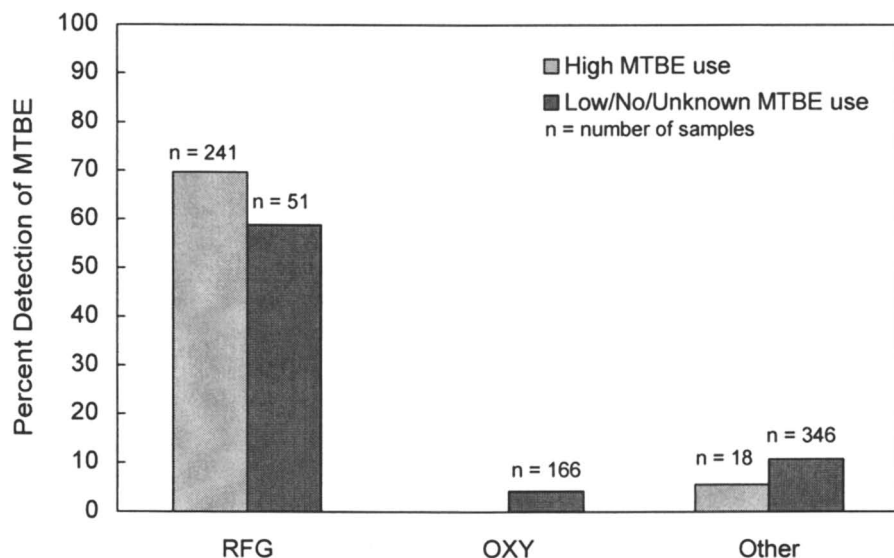(Reproduced with permission from reference 7. Copyright 1999 ACS Division of Environmental Chemistry.)

Figure 4. Frequency of detection of MTBE in samples of surface water (1993-2000) by MTBE use category (minimum concentration of 0.2μg/L) [NOTE: no samples were available for high-use OXY areas].
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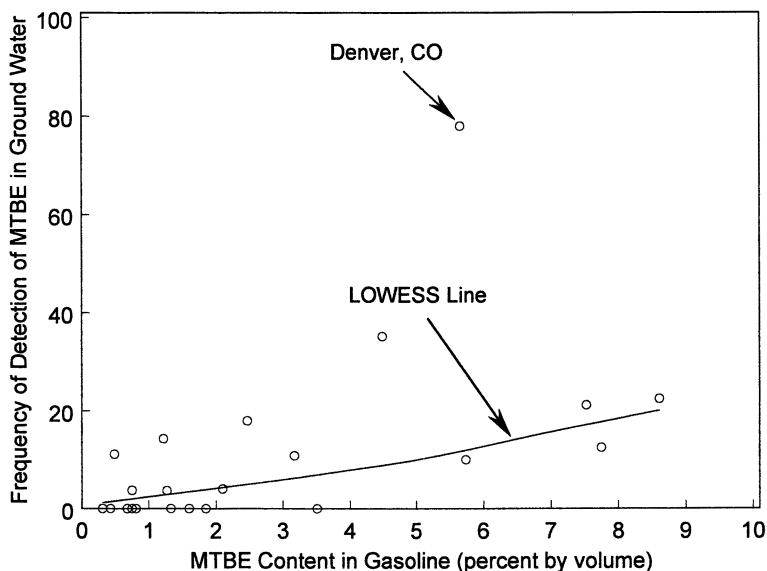
Figure 5. Detection frequency of MTBE in ground water (1993-2000) versus MTBE content in gasoline.
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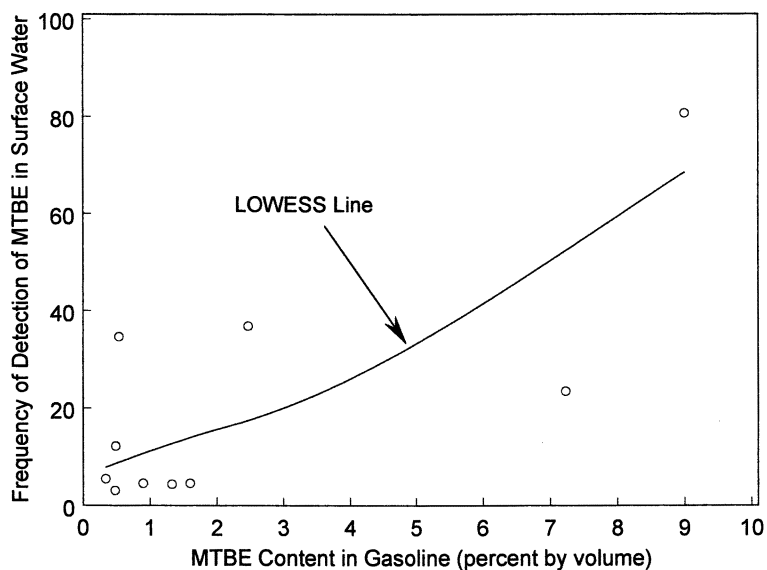

Figure 6. Detection frequency of MTBE in surface water (1993-2000) versus MTBE content in gasoline.
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Table II. Metropolitan areas where NAWQA has sampled ground and surface water for MTBE and where data exists on MTBE content in gasoline.

Ground Water	Surface Water
Albuquerque, NM	Columbia, SC
Atlanta, GA	Detroit, MI
Columbia, SC	Harrisburg, PA
Dallas/Fort Worth, TX	Memphis, TN
Denver, CO	Minneapolis, MN
Detroit, MI	New York, NY
Harrisburg, PA	Philadelphia, PA
Hartford, CT	Pittsburgh, PA
Indianapolis, IN	San Antonio, TX
Las Vegas, NV	Seattle, WA
Memphis, TN	
Miami, FL	
Minneapolis, MN	
New York, NY	
Norfolk, VA	
Philadelphia, PA	
Phoenix, AZ	
Pittsburgh, PA	
Portland, OR	
Reno, NV	
San Antonio, TX	
Seattle, WA	

MTBE in surface or ground water but was not sampled by any gasoline survey, the area was not included in figures 5 or 6.

The LOcally WEighted Scatterplot Smoothing (LOWESS) lines in Figures 5 and 6 represent predicted values of the response variable (frequency of detection of MTBE) based on the input variable (MTBE content in gasoline) using a weighted least-squares regression. A LOWESS line aids in emphasizing how the two variables are related without assuming a linear relation. The smoothness factor (f), or span, used for the LOWESS lines in both Figure 5 and 6 was 1.0 and thus the line represents a single weighted least-squares regression function.

The LOWESS line in Figure 5 indicates that increasing frequency of detection of MTBE in ground water in 29 metropolitan areas is related to increasing MTBE content in gasoline. Although the variability in MTBE frequency of detection seems to increase as MTBE content in gasoline increases, especially for ground water, the general trend is clear. One distinct outlier is present in the data. For surface water (fig. 6) the relation is more pronounced although there are fewer data points. For the same percent volume of MTBE in gasoline, the LOWESS line shows a higher detection frequency for surface water compared to ground water.

The frequency of detection of MTBE in ground water in the Denver, CO metropolitan area is substantially higher (79%) than any other area. This is probably a function of the shallow, vulnerable aquifer sampled in the Denver area and historically high use of MTBE. In 1987, Denver began a wintertime Oxygenated Gasoline program using MTBE. In 1989, Phoenix, Las Vegas, Reno, and Albuquerque also began wintertime Oxygenated Gasoline programs using MTBE. Although the NIPER data does not provide data earlier than 1990, it is presumed that substantial amounts of MTBE were used in these areas before this date. The historical use of MTBE in certain areas and lack of information on MTBE content in gasoline confound relational analyses by reducing the long-term arithmetic mean of MTBE content in these areas.

The relations illustrated in Figures 5 and 6 indicate that the frequency of detection of MTBE in surface and ground water has a positive relation to content of MTBE in gasoline. As the NAWQA program gathers more water quality and ancillary data, understanding of the relations between MTBE detection in water and various explanatory factors will be enhanced. Although the shape and slope of the LOWESS lines shown in these figures may change as more cities are studied, it is believed that the general trend in the data will not.

It is apparent that the occurrence of the fuel additive MTBE in surface and ground water is related to its use in gasoline. The frequency of detection of MTBE is higher in areas that use greater amounts of MTBE in gasoline. In fact, there is 2- to 5-fold increase in MTBE detection frequency in ground water in RFG or OXY areas that use MTBE as a gasoline oxygenate. For surface water,

the use of MTBE in RFG results in only a slight increase in the detection frequency of MTBE in RFG areas. As the percent by volume of MTBE in gasoline increases, the frequency of detection of MTBE in ground and surface water increases. Even at relatively low content of MTBE in gasoline ($\leq$ 2 %), such as areas in which it is used only as an octane enhancer, the frequency of detection of MTBE in surface water can be large.

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Chapter 2

Nonpoint Source Methyl *tert*-Butyl Ether Movement through the Environment: Ultra-Low Level (ppt) Measurements in California

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To achieve a 15 parts per trillion (ppt or 15 ng L^{-1}) detection limit for Methyl-*tert*-butyl-ether (MTBE), a method was developed using a purge and trap, gas chromatographic mass spectrometer (GC/MS) operated in the selected ion monitoring mode. We traced nonpoint source MTBE in precipitation, surface water, and groundwater that would have been undetected in previous studies with typical detection limits between 0.2 to 1.0 $\mu g\ L^{-1}$. MTBE is ubiquitous as a nonpoint source contaminant that persists through a variety of transport pathways at concentrations usually below current health advisory levels (i.e. 20-40 $\mu g\ L^{-1}$ for drinking water).

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Introduction

The fate of the fuel oxygenate MTBE in the environment is the focus of this contribution because it resists degradation and preferentially partitions into the water phase compared to other volatile organic compounds (VOCs). For example, the temperature dependent Henry's Gas Law constant, the ratio between air concentration and water concentration, at 15 °C for MTBE is low (0.011) compared to 0.17 for benzene or 0.39 for perchloroethylene (*1*). Viewed another way, 50,000 mg L^{-1} of pure liquid MTBE is soluble in water compared to 1,780 mg L^{-1} of pure liquid benzene (*2*). When it rains, MTBE in the atmosphere will partition into the rain as it falls at concentrations governed by the ambient atmospheric concentration, the temperature, and Henry's Gas Law constant -we use the term "washout" for this process.

Since the 1970s, when MTBE was introduced as an octane replacement for tetraethyl lead, MTBE use has grown and is currently added to 30% of the United States reformulated gasoline supply (*3*). Long-term health effects from MTBE are not known, but the U.S. Environmental Protection Agency (EPA) classified it as a possible carcinogen and a breakdown product, *tert*-butyl alcohol (TBA), is a carcinogen in laboratory animals (*4,5*).

Nonpoint source MTBE in surface water can come from a) washout of atmospheric MTBE, b) from street and parking lot runoff during rain events, and c) recreational boating on surface water bodies. This is distinguished from point source MTBE studies (e.g. leaking underground fuel tanks) both by its sources, and because point source MTBE is present at much higher concentrations. This study uses a significantly lower detection limit than previous studies (15 ng L^{-1}), to examine the distribution and behavior of nonpoint source MTBE in the environment.

As human activities increase levels of MTBE in the atmosphere, the ability to predict the fate and transport of MTBE in the environment will become a necessity. Nonpoint source contamination is a difficult problem to remediate when compared to point-source pollution, where responsible parties are easier to identify and remediation techniques are focused on a local scale.

By far, the largest sources of MTBE to the atmosphere are tailpipe emissions (50 million kg yr^{-1}), through evaporative emissions (18 million kg yr^{-1}), at petroleum refineries (1.4 million kg yr^{-1}), and 0.6 million kg yr^{-1} from refueling at gasoline stations (*6*). A higher percentage of these activities occur in urban areas, and that is where atmospheric washout could be a nonpoint source of MTBE into surface water and groundwater. According to the 1990 United States Census 75% of the population lives in urban areas defined as population centers with greater than 2,500 people (*7*). Therefore, 75% of the population of the United States, that relies on potable water derived from local surface and groundwater sources, potentially could be affected by nonpoint source MTBE.

More frequent monitoring and modestly lower detection limits have increased MTBE detection in surface water. For 592 storm water samples

collected in 16 United States metropolitan areas, MTBE was detected in 7% of the samples (8). During the course of the above study, the minimum reporting level (MRL) changed from 1.0 µg L^{-1} (83% of the samples) to 0.2 µg L^{-1} (6% of the samples). Surface water samples collected from Long Island, New York using a MRL of 0.5 µg L^{-1} resulted in a 29% detection frequency (9). However, in a study with a lower detection limit of 0.2 µg L^{-1}, MTBE was detected 100% of the time for 14 New Jersey surface water samples (9). Approximately 55% of potable water consumed in the United States is surface water (10), and therefore MTBE has a high potential of being mixed into potable water distribution systems.

Natural attenuation studies give conflicting results with laboratory studies (11, 12) in concluding that MTBE is recalcitrant under aerobic, anaerobic and reducing conditions. Other studies present convincing evidence for microbial degradation of MTBE (3, 13). A large national survey of groundwater samples from eight urban areas found that chloroform followed by MTBE were the most frequently detected volatile organic compounds (14), suggesting low attenuation rates.

We present data from California using a new lower detection limit of 15 ng L^{-1} in order to trace the fate of MTBE through aqueous phase reservoirs of the environment. The objectives of this study are twofold – to examine the regional spatial distribution of MTBE in surface waters using the lower detection limit of 15 ng L^{-1}, and to look for evidence of non-conservative behavior of MTBE in the surface and near surface environment. The latter goal was accomplished by examining the pattern displayed by MTBE concentration during a storm runoff event, and by measuring MTBE in recharging surface water and groundwater.

Method for Part Per Trillion (ppt) Detection of MTBE

Details of this method have been presented elsewhere (15), but briefly, a purge and trap unit (model 4460A, OI Analytical, College Station TX) connected to a model 5970B (Hewlett-Packard, Palo Alto, CA) GC/MS was operated in the selected ion monitoring mode for low level MTBE determination (15 ng L^{-1} detection limit). The initial samples in this study were spiked with an internal standard of 10 µL of 2.5 ng µL^{-1} bromofluorobenzene and the remaining samples were spiked with 10 µL of 0.4 ng µL^{-1} d12-MTBE in methanol. A Teflon-coated stirrer was added to a pre-cleaned VOA vial to which 25 mL of sample plus 10 µL of internal standard were added. Ultra High Purity helium purged the stirring (40°C) sample at 40 cc min^{-1} for 11 minutes. A charcoal, Tenax, and silica gel (#6 OI Analytical) trap collected the analytes. The analytes were then desorbed from the trap at 180°C for two minutes and introduced via a 110°C transfer line into the GC. Separation of analytes was accomplished with a 60 m RTX-502.2 GC column (Restek Corp., Bellefonte, PA) with a 0.32 mm inner diameter and a 1.8 µm film thickness.

The GC program was as follows: 2 minutes at 35°C followed by heating to 65°C at 5°C min^{-1}, then heated at 10°C min^{-1} and held at a final temperature of 280°C for 5 minutes. The trap was baked at 180°C for 20 minutes prior to each analysis. The selected ions listed in Table I were monitored for a dwell time of 100 ms and a MS cycle time of 1.1 seconds.

Blank samples and field blanks were prepared by boiling 18 MΩ water (Milli-Q, UV Plus system, Millipore, Bedford, MA) for 30 minutes. The cooled water was transferred to a 40 mL VOA bottle, leaving no headspace. Care was taken to minimize contact of the blank samples with the atmosphere because open vials that were exposed for several hours became contaminated with atmospheric MTBE.

Samples for this study include grab samples, taken in moving water, in 40 mL amber VOA vials with no headspace. Groundwater samples were pumped through Teflon-lined tubing. For each sampling period field blanks (prepared in the lab as described above) were taken along as a control. Field blanks were also established on deep, old groundwater collected in the Sacramento Valley, whose concentrations fell below the detection limit (*15*). All samples were stored at 4°C and most were analyzed within 4 days and all by 14 days.

Table I. Selected ion monitoring mode

Constituent	Ions of m/z
MTBE	43, 57, 73
d_{12}-MTBE	50, 66, 82
bromofluorobenzene	94, 96, 176
screen for VOA vial contamination	75, 76

A storage study was conducted to determine the ideal turnaround time for MTBE sample analysis. Figure 1 displays the results from measuring a series of 40 mL samples prepared with an initial MTBE concentration of 2.5 µg L^{-1} and stored at 4°C. The error bars for the storage study are much larger than for the samples presented in this study because this was early in the method development and the d12-MTBE internal standard had not yet been adopted. Approximately 20% of the initial MTBE was lost during a month of storage time. For optimal results, samples should ideally be measured within a week.

California: Nonpoint Source MTBE Fate and Transport

We present the fate and transport of MTBE initially from the perspective of a single watershed in central California, then expanded to several drainage

basins, and finally to a regional scale comparison of groundwater samples collected in two basins in central and southern California.
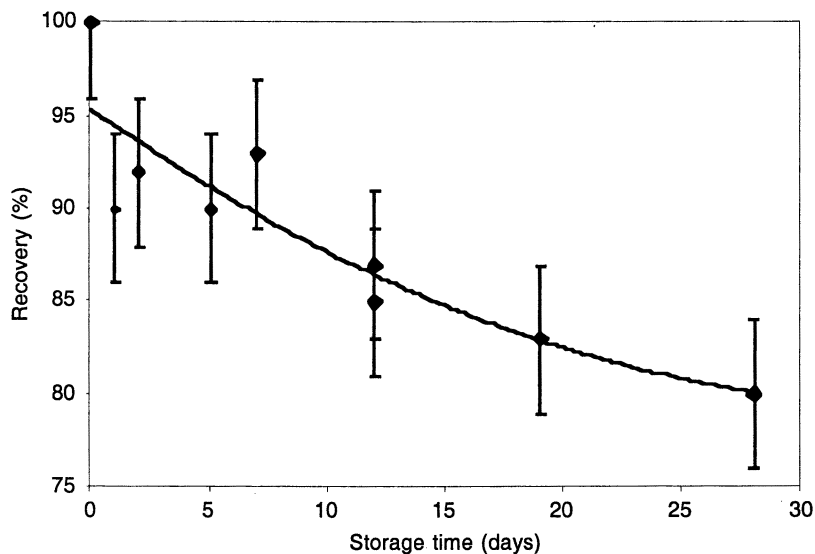

Figure 1. Results of the shelf life of MTBE in VOA bottles.

Two storm events were sampled at Niles Canyon, which is just upstream from the outflow location of the 1640 km² Alameda Creek Watershed (16) east of San Francisco Bay (location shown in Figure 3). This location was chosen for monitoring because the Niles Canyon station for Alameda Creek is the outflow location for the entire watershed and because precipitation causes a rapid flow response at Niles Canyon. Alameda Creek watershed comprises urban, agricultural, and undeveloped areas, with one tributary having a small flood-control dam. Only 7% of the watershed is zoned residential or commercial(16).

The MTBE concentration in precipitation sampled on three separate occasions from 1998-1999 ranged from 67 to 141 ng L^{-1}. This concentration range is consistent for atmospheric washout with the predicted and measured values of atmospheric MTBE concentration (6). During a runoff event in March 1999, the MTBE concentration of precipitation collected at the Niles Canyon site was 100 ng L-1 (Figure 2). Note that the sampling site is on the perimeter of urban areas of the San Francisco East Bay.

The MTBE concentration in runoff in March 1999 varied from <80 ng L^{-1}, before any significant increase in discharge, to ~100 ng L^{-1} at about five hours after peak discharge (Figure 2). The lag time between peak flow and peak

MTBE concentration suggests that either the peak discharge had contributions from "pre-event" soil water low in MTBE, or undeveloped parts of the watershed were dominant and urban runoff was delayed about five hours. Note that the peak MTBE concentration is closely associated in time with peak turbidity.
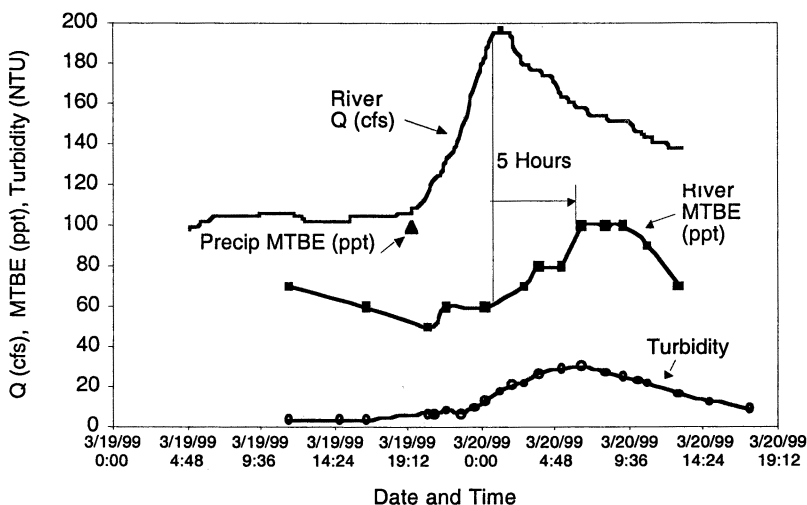

Figure 2. A small storm water runoff event in March 1999. Q is discharge.

The fact that the peak concentration in MTBE in the stream sample closely matches the MTBE concentration in the precipitation sample suggests that atmospheric washout is the nonpoint source and that overland flow dominates flow during a runoff event. Further evidence that precipitation and overland flow dominate MTBE occurrence in the stream, is that during a March 1998 flow event that had six times the discharge, the peak MTBE concentration was 85 ng L^{-1} and had a similar lag time as the March, 1999 event. In other words, the washout effect produced runoff of the same concentration that moved through the watershed simply at a higher volume of flow compared to the smaller storm event.

An expanded survey of major California rivers discharging into San Francisco Bay via the Sacramento-San Joaquin Delta was conducted periodically from 1998-1999 (Figure 3). The majority of locations sampled in June 1998 have higher MTBE concentrations than the Niles Canyon data
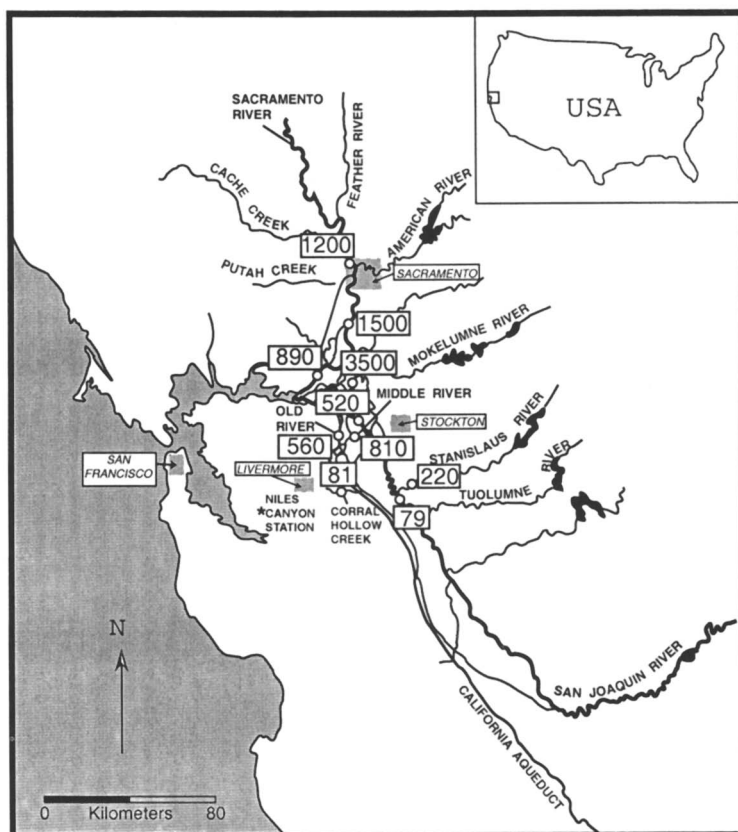
Figure 3. MTBE (ng L⁻¹) concentrations for surface waters collected in June 1998. Also shown is the location of the Niles Canyon station.
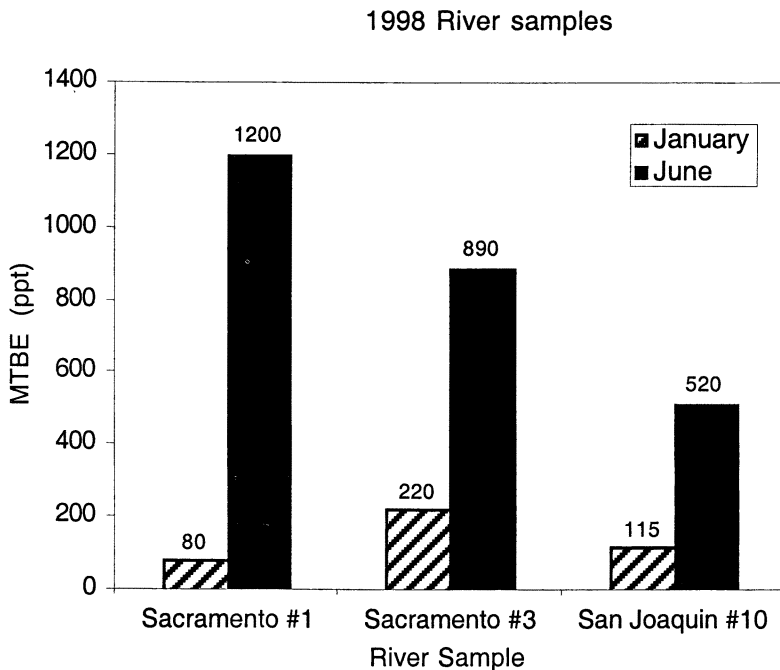
1998 River samples

Figure 4. Comparison of winter and summer MTBE samples.

(Figures 2 and 3). Only three locations sampled (Corral Hollow Creek, Stanislaus River and the southern San Joaquin River locations) could be grouped with the Niles Canyon station as being dominated by the atmospheric nonpoint source. The remaining surface water summer samples range between 520 and 3500 ng L^{-1}.

The most probable source for the enhanced summer concentrations of MTBE in surface water is recreational boating. Recreational boats have two-stroke or four-stroke engines that introduce relatively large quantities of both engine exhaust and incompletely combusted fuel. Boat engines also come in direct contact with the water giving the MTBE a direct path into the aqueous phase. In fact, the sample with the highest concentration, the 3500 ng L^{-1} Mokelumne river sample, was collected near a marina used for recreational boating. A survey over one year at Donner Lake produced a clear relationship between marina activities at the lake and MTBE concentration (17). Laboratory tests of engines found that aqueous emissions of MTBE from two-stroke engines are 24 times higher than a four-stroke engine (18). The two-stroke engine releases 3 to 10% of the MTBE in the fuel directly to the water (18).
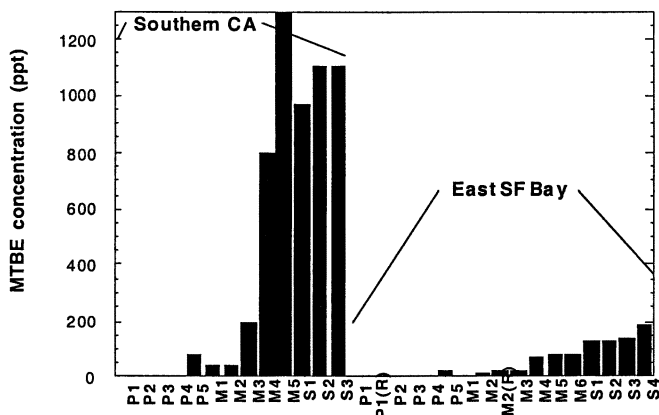
Figure 5. MTBE measurements in surface waters (S#), adjacent monitoring wells (M#) and nearby production wells (P#) for an East San Francisco Bay location and an urban Southern California location.

During the winter rainy season, recreational boating activity is minimal, and the MTBE concentrations were lower (Figure 4). The winter values are similar to that expected for washout of MTBE from the atmosphere.

We also collected groundwater samples in the East San Francisco Bay area immediately downstream from the Niles Canyon monitoring location, and from waters associated with the west coast injection barrier in Los Angeles (Figure 5). There is some evidence for non-conservative behavior of MTBE at the East Bay site. In an experiment to examine changes in water quality during infiltration, an inert tracer was introduced into the surface water bodies (S1 through S4) that provide recharge to the groundwater basin. Several water quality parameters, including MTBE, were measured in the surface water, in monitoring wells only a few meters from the ponds, and in monitoring and production wells further downgradient. Deeper samples in the recharge pond water had somewhat lower concentrations (116-127 ng L^{-1}) than shallow samples (133-142 ng L^{-1}). One monitoring well located just adjacent to a pond had a conservative tracer concentration that showed no dilution during recharge. However, the measured MTBE concentration was only 72 ng L^{-1}, significantly less than the levels measured in the pond (>100 ng L^{-1}), suggesting degradation, retardation, or mixing with water of lower MTBE concentration. Decreases in MTBE concentration measured in wells further downgradient was consistent with simple dilution based on the independent inert tracer results.

In the southern California waters, the surface waters collected in June comprise California Aqueduct water, reclaimed wastewater, and a blend of these two sources (*19*). Note that these surface water concentrations are higher than the surface water samples in the previous East Bay example, but similar to summer runoff values measured in northern California rivers. The southern California groundwater samples were collected in urban/industrial areas having a local oil refinery, and they were recharged by injection from the surface water sources. The MTBE concentrations in these groundwaters are higher than in the East Bay example. Local point sources may contribute some of this MTBE. For example, one production well water had a pre-industrial age determined from tritium and radiocarbon measurements (*19*). However, the MTBE concentration was ~100 ng L^{-1}, suggesting a small contribution from a high concentration source.

Conclusions

MTBE is ubiquitous in surface waters when measured at the low level detection limit (15 ng L^{-1}). All major rivers sampled in northern California (i.e. the major tributaries to San Francisco Bay) had measurable MTBE concentrations. The winter surface water concentrations can be explained by washout of atmospheric MTBE by precipitation, while summer surface water MTBE concentrations were elevated due to recreational motor boats.

The low level measurement method developed for this study allowed us to examine transport properties of MTBE to check for non-conservative behavior. A tracer study of an East San Francisco Bay groundwater basin provided evidence for retardation or degradation of MTBE between the surface water body that directly recharges groundwater followed by conservative transport of MTBE further downgradient. This suggests that MTBE remains recalcitrant as it flows through a groundwater basin, at least on the time scale of this study (one year).

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Chapter 3

Methyl *tert*-Butyl Ether at California Leaking Underground Fuel-Tank Sites: Observations and Implications

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The goal of this work is to examine data from a large population of real-world LUFT sites in California in order to investigate the in-situ behavior of MTBE vs. BTEX using simple statistical techniques. Concentration trends in terms of mean behavior and variability are explored in detail based on extensive data from 480 sites spanning 1996 through 1999. Observations are found consistent with expectations based on MTBE's physical and chemical properties. MTBE concentrations in the field are found to be increasing and highly variable compared to BTEX. In addition, MTBE attenuation is observed to be significantly limited compared with benzene.

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Background

MTBE is a common and widespread contaminant in groundwater at leaking underground fuel tank sites (LUFTs). Widespread use of this compound as a fuel oxygenate added to gasoline to reduce air pollution and increase octane ratings has resulted in frequent detections in samples of shallow groundwater from urban areas throughout the United States (1). In California alone, it is estimated that at least 10,000 LUFT sites have been impacted to some degree by MTBE (2).

Due to differing characteristics, MTBE is expected to present distinct management challenges compared to traditional fuel contaminants such as the aromatic hydrocarbons (BTEX). Both the solubility of pure MTBE and its mole fraction in California reformulated gasoline are order of magnitude greater than that of benzene, approximately 50,000 mg/L versus 1,780 mg/L and 0.12 versus 0.015, respectively (3). Consequently, the solubility of MTBE and benzene in water saturated with California reformulated gasoline may be as high as ~6,000 mg/L and ~27 mg/L, respectively. In addition, the organic-carbon-based partition coefficients are approximately 11 and 80 for MTBE and benzene, respectively, so very little significant retardation of MTBE compared with benzene may occur during their transport in the saturated zone (3). Also, MTBE (and other alkyl ether fuel oxygenates) biodegrade much less readily than benzene. To date, field data and microcosm studies indicate that MTBE, compared to benzene, may be resistant to intrinsic biodegradation at the majority of LUFT sites.

The goal of this work is to examine LUFT data, in light of the above differences, from a large population of real-world sites in order to investigate the in-situ behavior of MTBE vs. BTEX using simple statistical techniques. It is of practical importance to determine the general patterns of MTBE behavior compared to BTEX as it is manifested at real world sites to provide a means of field validating conceptual models of contaminant distribution and transport. It also provides examples of the range of situations that may be encountered by workers in the field.

This study is based on data submitted by various petroleum industry sources from 480 LUFT sites located primarily in Los Angeles and Santa Clara County. These sites include 4,652 monitoring wells with a history of 32,414 sampling events that include MTBE results and span late-1995 through mid-1999. This excludes samples reporting free-product in order to focus only on dissolved plumes. The sites are assumed typical of the LUFT sites found on alluvial deposits throughout California's high population density regions. For the study, sampling results were included only when both BTEX and MTBE results were available. Thus, past histories of hydrocarbons observations are omitted to avoid past sampling bias and to limit the focus of this work to comparative assessment.

Comparison of MTBE and BTEX Concentrations.

In this study, four examples of statistical analysis of MTBE and BTEX observations are considered. First, Temporal trends in the distribution of maximum benzene and MTBE concentration for a collection of individual sites is evaluated to determine the concentration levels observed in the field and to see if there are associated temporal trends over the study period. Next, the issue of concentration variability is addressed using a modal decomposition of contaminant concentration levels using principal component analysis (PCA) that provides a quantitative description of inter-compound variability. The issue of concentration variability is then further explored in the time domain by observing overall mean concentration trends over time with respect to seasonal hydrographic fluctuations. Finally, well specific trends are investigated using relative concentrations of MTBE and BTEX demonstrating potential limits for natural attenuation of MTBE versus benzene.

Maximum Concentration Distributions

Recent increases in MTBE usage should have resulted in higher observed concentrations because it is assumed that many fuel distribution systems continue to leak. Maximum Concentrations of MTBE and benzene were compared by year using cumulative distributions too see if this was the case. The cumulative distribution gives the likelihood of Maximal concentrations at LUFT sites not exceeding a given concentration level. The distribution of maximum observed benzene concentrations was found to be relatively consistent throughout the study period. Alternatively, the distribution for MTBE showed an increase in maximum observed concentration of nearly tenfold at all percentiles. Examples for the 10th and 90th percentiles are shown in Figure 1; 10% and 90% of sites have maximum concentrations not exceeding the plotted concentrations.

To consider MTBE a new groundwater contaminant is incorrect bearing in mind its use in gasoline formulations, at lower concentrations, since the late 1970s. This is evident in figure 1 considering that as early as 1995, the beginning of the California RFG program, a full range of maximum concentrations was observed. This can be attributed to wintertime use of high concentrations of MTBE as early as 1992 and its use as an octane enhancer beginning in the late 1970s (4). Of particular note is the monotonic increase in maximum MTBE concentrations seen every year through 1999 at all percentiles. The introduction of MTBE in all California gasoline at higher concentrations appears to have resulted in as much as a tenfold increase in maximum observed MTBE concentrations to date at California's LUFT sites. No overall trend can be seen in maximum benzene concentrations. Results not presented here indicate that the same general trend occurs when overall mean concentrations are considered instead of maximums.
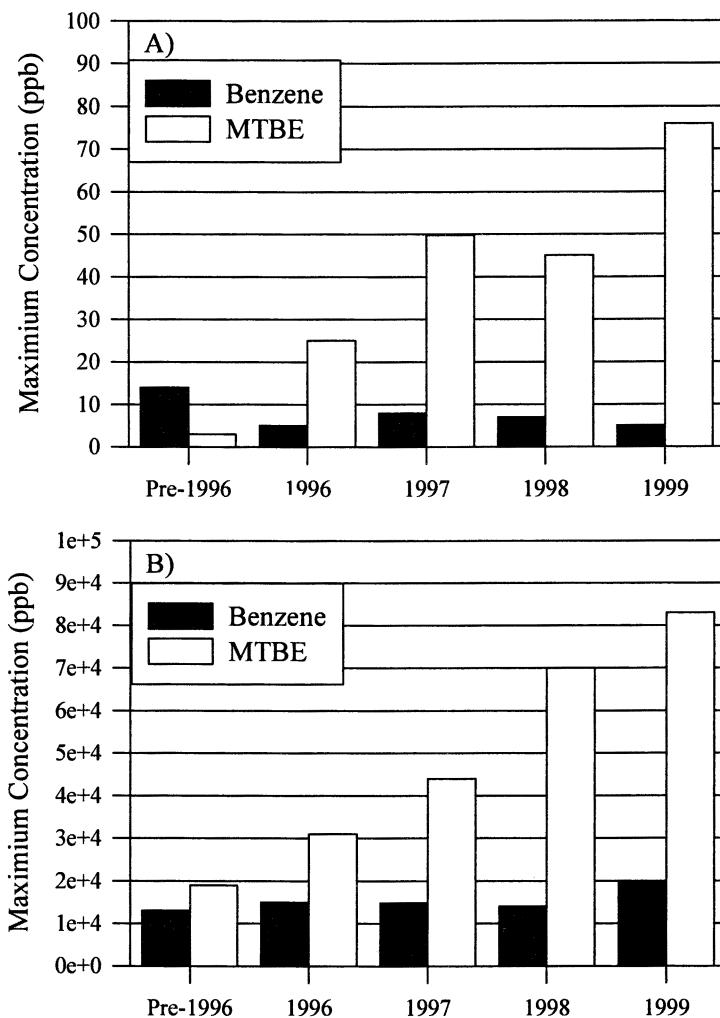
Figure 1. Comparison of maximum observed benzene and MTBE concentration from 480 California LUFT Sites by year from pre-1996 through 1999. Results are shown for both a) low and b) high concentration percentiles, the 10th and 90th respectively.

Modal decomposition of BTEX and MTBE covariability using principal component analysis (PCA).

In addition to investigating the magnitude of observed concentrations at LUFT sites, variability was also considered in order to quantify the similarity between BTEX compounds and the uniqueness of MTBE. Principle component analysis (PCA) was used to quantify the dominant modes of contaminant variability between MTBE and BTEX. PCA is a common statistical technique used in both the social and earth sciences to determine the most efficient combinations of variables to describe variability within a data set (Jolliffe, 1986). Rather than treating BTEX and MTBE concentrations as five independent variables PCA allows the variability to be distributed among combinations of these variables which most efficiently describe variability in the least squares sense. Thus, the first component explains the maximum portion of the data variance possible using a single combination of variables. The second explains the maximum portion of the remaining variance and so on.

Principle components are easier to understand in concept than mathematically. Only a brief and admittedly incomplete explanation is provided here. Consider each of the five compounds of interest to be represented by an independent axis. Each set of concentration observations can then be thought of as a point in 5-dimensional space. Basic linear algebra allows for an infinite number of possible sets of orthogonal axes that can represent this point. This is accomplished through any rigid rotation of the concentration axes. When rotated each axis no longer need represent a single compound but a linear combination of compounds. PCA uses a particular coordinate rotation defined by the eigenvectors of the concentration covariance matrix. The resulting linear combinations of variables, or components, represent directions of maximum uncorrelated variability. The sum of concentration variance over all of the components is equivalent to the total variability of the original data.

For groundwater concentration data in this study, log-transformed data was used to produce less skewed concentration distributions avoiding bias caused by infrequent high concentrations many orders of magnitude greater than the lowest observations. All of the log-transformed variables have similar ranges and distributions and, as a result, contribute nearly equal variance to the complete dataset (~20% each).

PCA indicates that 90% of the total variance can be explained using only the first two of five variables, which are shown in figure 2. The first variable, accounting for 73.4% of total variance, shows a small MTBE contribution that varies with BTEX suggesting a small but quantifiable correlation. Alternatively, contributions across BTEX are large and consistent indicating that log BTEX concentrations are strongly correlated. The second variable, accounting for 15.2% of the total variance, has a strong MTBE contribution and minimal
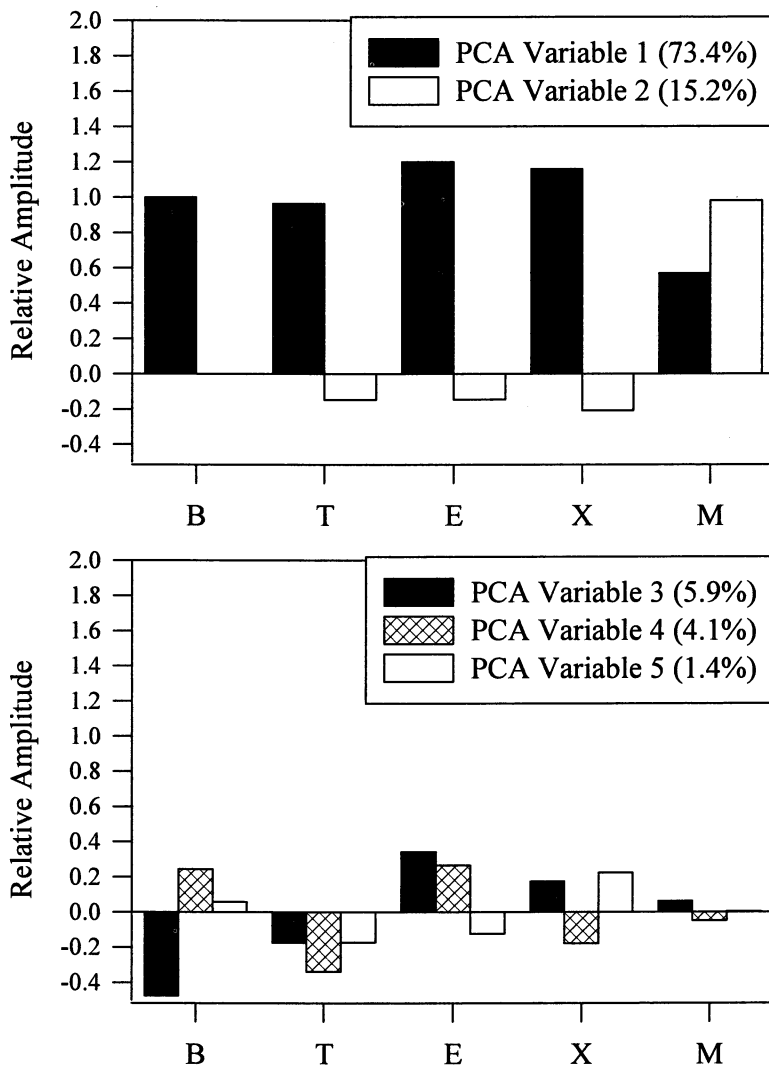
Figure 2. Principal components (variables) derived using PCA. The magnitude of each individual variable is scaled by its standard deviation in order to represent the variable's contribution to log concentration fluctuations. The variables contribution to total variance is given by the legend percentages.

contributions from BTEX. This variable accounts for the approximately 2/3 of all MTBE variability and is nearly independent of BTEX concentrations. This clearly demonstrates the uniqueness of MTBE observed in the field compared against BTEX compounds that behave very similarly with one another. The remaining three variables combined amount to only 11.4% of total variability and explain inter-BTEX variability (the portion of the BTEX concentration variance that does not vary with itself or MTBE as in the first variable or with MTBE as in the second).

Temporal trends in benzene and MTBE mean concentration compared with changes in local hydrography.

In addition to the concentration inter-variability described in the previous section, MTBE concentration variability over time was examined in response to hydrographic variation and compared with that of benzene. To do this the maximums of observed MTBE and benzene concentrations at all sites and wells were time averaged by monitoring quarter using geometric means. The resulting concentration trends compared with monthly rainfall and average fluctuations in water table depth are shown in Figure 3. The monthly rainfall series is taken from the Los Angeles Civic Center meteorological record. This record was found to be similar (correlation coefficient of 0.92) with that of the City of San Jose and therefore considered representative of both the Northern California and the Southern California sites. Fluctuations in water table depth are defined as the deviation in depth to water in each well relative to the well's average water depth over time. All Quarterly and monthly values are plotted at the midpoint of their respective sampling periods.

The figure shows that average deviations in water depth are strongly related to seasonal precipitation such that increases in water table depth begin with the termination of seasonal rainfall in the spring (second quarter) and begin to rise shortly after rains begin in the late fall (fourth quarter). Over the 14 quarters shown, mean maximum benzene concentrations are uniform at approximately 2500 ppb. Small decreases in concentration are observed at minimum water depths and are likely the result of dilution as at these times well screens sample a longer water column of fresher water. This is particularly evident during the unusually wet el nino year of 1997/98. Subsequent increases in concentration are seen once infiltrated waters have time to interact with and mobilize contaminants from source areas.

MTBE shows a similar trend with two significant differences. First, oscillations in mean maximum concentration are on the order of thousands of parts per billion compared with hundreds for benzene. This is likely the result of
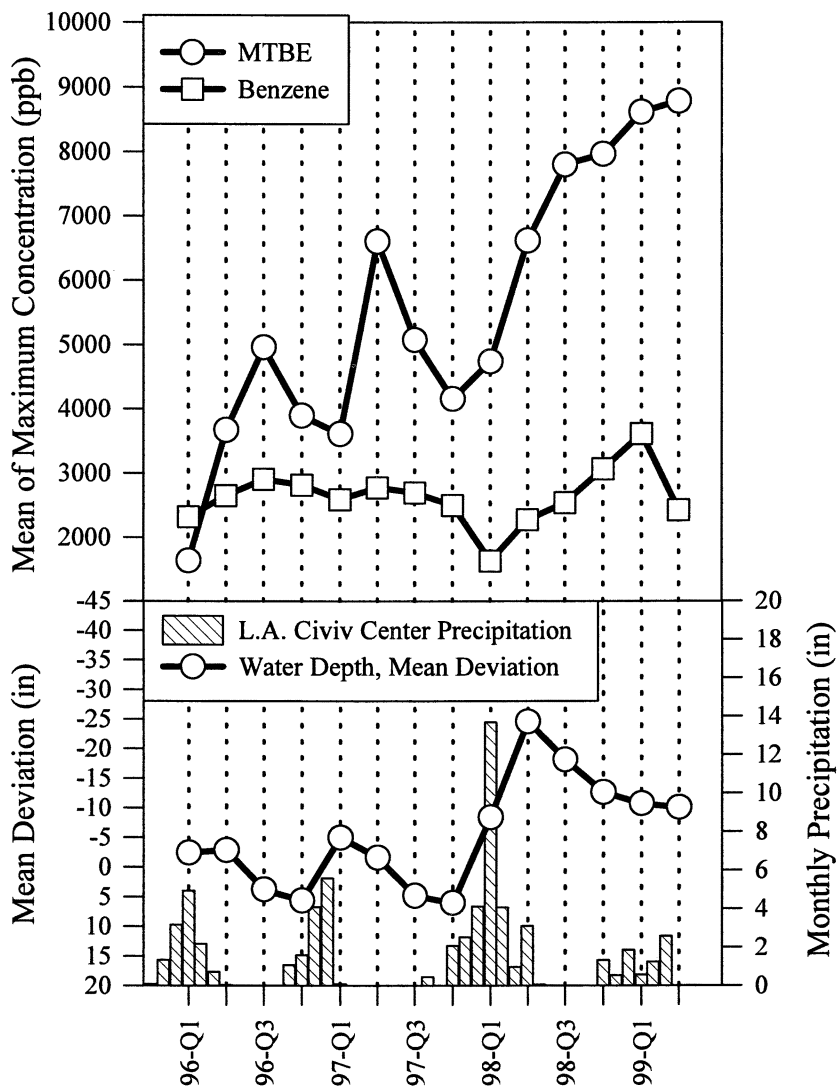
Figure 3. Mean concentration trends (480 sites) by quarter compared with representative hydrographic variability (Los Angeles). Year and quarter are given on the x-axis.

MTBE's high mobility; in dissolved phase MTBE does not become smeared throughout the subsurface like benzene but moves unpredictably with the groundwater. Also, MTBE concentration oscillations are superimposed on an overall upward trend of nearly an order of magnitude. With every rise and fall of the water table, higher concentrations of MTBE are observed. This is most simply explained by an increase in source concentration following the switch to year-round use of reformulated gasoline.

Relative concentration distributions.

Relative concentrations were used for a simple assessment of relative attenuation of MTBE and TEX versus benzene. Although this data is insufficient for a detailed analysis of mechanisms, it is useful for observing gross differences between these compounds. Research involving MTBE attenuation occurs mainly in the laboratory but it is important to validate conceptual findings in the field setting. Unfortunately, the level of detail and site specificity available in a laboratory setting is not possible here and this investigation is limited to a crude assessment of general field behavior.

Concentration values were included from the entire dataset providing all contaminant species were observed above detection limits. Thus the analysis is limited to samples taken from locations during periods when all contaminant plumes were present and quantified. Concentrations were compared sample to sample to control for static environmental effects (equivalent subsurface characteristics and hydrologic forcing. Confounding dynamic effects (unknown source distribution and composition history) are unavoidable and add variability to any underlying functional relationship between contaminant attenuation due to compound properties alone. The analysis is also limited to relative attenuation as opposed to absolute attenuation because overall concentration trends are compared with each other as opposed to the more problematic variables of space or time.

Relative concentrations of MTBE and TEX (toluene, ethylbenzene, and xylenes), compared to benzene (divided by benzene concentration), were considered in relation to absolute benzene concentration. As benzene concentrations vary across samples, how do the concentrations of MTBE and TEX vary compared to benzene? A summary of the relationship is given in figure 4. Geometric mean values of relative concentrations, grouped by ranges of benzene concentration, are shown with benzene concentration ranges decreasing by order of magnitude. If a given compound and benzene have equivalent attenuation characteristics then the relative concentration of that compound compared to benzene should be constant as a function of absolute benzene concentration. Compounds with greater attenuation potential than benzene will show a decrease in relative concentration as absolute benzene concentration decreases. Conversely, compounds that attenuate less redily will show an increase in relative concentration as benzene concentration decreases.
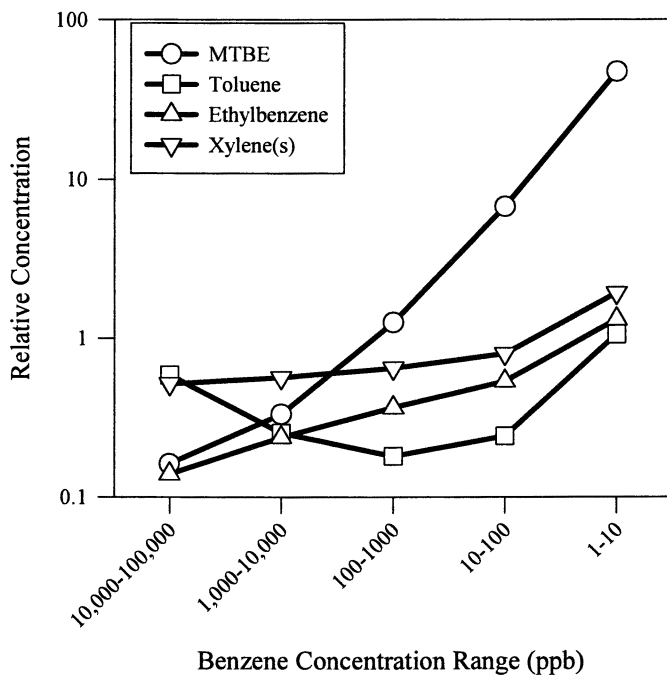
Figure 4. Relative concentrations compared with absolute benzene concentration. Relative concentration of a compound is defined as that concentration divided by benzene concentration on a well by well, sample by sample basis.

In general all compounds show increasing relative concentrations with decreasing benzene concentration. This indicates that as benzene concentrations decrease, concentrations of the other compounds do not show as significant a decrease. Benzene appears to have the greatest attenuation potential compared with TEX or MTBE. The only exception is for toluene at high benzene concentrations, in which case relative concentration decreases with absolute benzene concentration. This may suggest that toluene is degraded preferentially to benzene in high concentration, low dissolved oxygen, near source regions.

Although all compounds show less relative attenuation than benzene, the difference between MTBE and TEX is obvious. Over the range of absolute benzene concentrations (five orders of magnitude), relative TEX concentrations change by a maximum of a factor of ten. For instance, on average, as benzene concentration decreases five orders of magnitude such as from 10,000 to 1 ppb, ethylbenzene concentration decreases by about four orders of magnitude equivalent to a decrease from 10,000 to 10 ppb. Alternatively, MTBE relative concentrations increase by nearly four orders of magnitude over the given benzene concentration range. For comparison, this suggests a decrease in MTBE concentration on the order of 10,000 to 500 ppb compared to the decrease in benzene of 10,000 to 1 ppb. Thus, MTBE appears to attenuate less significantly than benzene. Likewise, MTBE also attenuates less significantly than TEX.

Note that at the highest benzene concentrations, average MTBE relative concentrations are only approximately 0.2. However, at the lowest benzene concentrations, average relative MTBE concentrations are about 50. Thus at the highest benzene concentrations, MTBE concentrations are comparatively lower and at the lowest benzene concentrations MTBE concentrations are much higher. Higher relative MTBE concentrations occurring with low benzene concentration is not surprising and can be explained by preferential degradation of benzene. Lower relative concentrations of MTBE occurring with high benzene concentrations is counterintuitive considering MTBE's greater solubility and higher maximum concentrations as shown in figure 1. This observation suggests an important difference between mean concentrations and maximums. While maximum MTBE concentration is on average greater than benzene, average MTBE concentration is generally lower than benzene (for samples with high benzene concentrations). This implies that the highest MTBE concentrations are more limited in spatial extent than the highest benzene concentrations. A possible contributing mechanism is the relatively rapid dissolution of MTBE from NAPL source zones as a result of its high solubility. This phenomenon is expected to be significant only at those sites where releases have been reduced or terminated. Considering the general observation of increasing maximum concentrations over time, it is unlikely that this has occurred at the majority of sites.

Summary

Analysis of the field data collected for this study confirms the fundamental differences between BTEX and MTBE contamination. In particular, solubility and source history lead to differences in average concentration trends. The higher solubility of MTBE compared to benzene and its recent increase in use has led to higher observed concentrations. Maximum benzene concentrations have been stable across the population of study sites during the study period. Maximum MTBE concentrations have increased as much as an order of magnitude since 1995. No evidence for the stabilization of maximum MTBE concentrations has yet been observed. Also, the majority of BTEX variability is correlated indicating the similar properties and behavior of these compounds (PCA variable 1). On the contrary, the majority of MTBE variability is independent of BTEX variability indicating significantly different properties and behavior (PCA variable 2).

Local hydrological processes influence mean variation in benzene and MTBE concentrations. Seasonal precipitation events followed by water table fluctuations have a much more pronounced effect on mean MTBE concentration compared with benzene. The benzene trend consists of small mean concentration fluctuations (200-1000 ppb) overlaying a consistent mean concentration of approximately 2500 ppb. The MTBE trend consists of relatively large fluctuations (3000-4000 ppb) superimposed on an upward trend (1000 to 9000 ppb from early-1996 to mid-1999). Large swings in observed MTBE concentrations throughout the state should be expected in the future. For all compounds and especially for MTBE, significantly reduced concentrations during extended periods of low water table levels should not be mistaken for attenuation. This problem will be even more important on a site-by-site basis where statistical noise is far greater resulting in unexpected and dramatic concentration fluctuations. Investigators should be certain to look for functional relationships between concentration trends and water table fluctuations before assuming that concentration reductions are truly indicative of attenuation.

Relative concentrations demonstrate that on average attenuation of MTBE concentrations within existing monitoring networks is limited compared to BTEX. As benzene concentration varies, relative concentrations of TEX remain relatively stable. Thus, TEX concentrations vary with benzene, although TEX shows a slight reduction in attenuation potential. As benzene concentrations decrease, relative concentrations of MTBE increase substantially. Thus, as benzene concentrations decrease by five orders of magnitude, MTBE concentrations decrease by just greater than one. The most likely explanation for this observation is differential biodegradation. If biodegradation is absent or severely constrained within observed monitoring networks then all or most of the observed attenuation must result from mechanical mechanisms such as

dispersion and volatilization.   Unfortunately, the existence of MTBE biodegradation or lack thereof cannot be determined form the available concentration data and no assumptions can be made regarding behavior downstream of existing monitoring locations. However, even if biodegradation can not be quantified using the available information, it is clearly constrained relative to benzene and TEX which are know to be commonly biodegraded in the subsurface.

MTBE is clearly a very different contaminant compared with BTEX. It behaves individually whereas BTEX acts together.   It is seen in higher concentrations with considerably greater independent variability over time. In addition, attenuation appears to be much more limited within existing monitoring well networks.   Attenuation of MTBE may be dominated by mechanics.   In contrast, attenuation of BTEX, especially benzene, is often dominated by biodegradation kinetics. As a result, the field worker can expect to see higher MTBE concentrations and large unexpected concentration fluctuations. Overall MTBE concentrations are expected to increase until its use and consequential releases to the environment are reduced.   Its fluctuations and anomalous behavior will be evident for many years to come until sources are depleted and whatever attenuation mechanisms available have run their course. Every year additional mass will be mobilized through infiltration and water table fluctuations.   The eventual fate of MTBE contamination of groundwater will depend ultimately on biodegradation. It does not appear, based on this simple evaluation, that biodegradation will be capable of mitigating MTBE contamination on the most local scales.

Finally, the observations presented above and taken as a whole, confirm the fact that BTEX and MTBE are fundamentally different contaminants with commonality limited mainly to the geographic distribution of releases. However, even this similarity is not without exception based on the fact that BTEX plumes are not always found to have an associated MTBE plume and vice-a-versa. BTEX-only plumes may indicate the absence of a recent release. On the other hand MTBE-only sites may suggest either an undiscovered but spatially limited and/or rapidly degrading BTEX plume or a vapor-only source. Observations suggesting these possibilities have been documented at many typical LUFT sites. These extreme examples further indicate the fact that LUFT sites do not simply have "gasoline" plumes. Rather, they are characterized as having two significant types of dissolved plumes, aromatic hydrocarbons as distinguished from MTBE, which will often appear to behave independently. Past or present observations of one type of plume will often be an insufficient basis for making assumptions regarding the other.

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Opening Pandora's Box: Overview of States' Responses to the Methyl *tert*-Butyl Ether Enigma

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State program responses to the widespread impacts of methyl tertiary butyl ether (MTBE) contamination in ground water have varied considerably. Some states have set cleanup levels based on the U.S. Environmental Protection Agency (EPA) drinking water advisory levels of 20-40 ug/L (micrograms per liter), some have used risk-based approaches to set site-specific cleanup levels, and others have adopted their own cleanup or action levels. In 1997, 18 states had cleanup or action levels for MTBE. By 2000, the number of states with cleanup or action levels for MTBE had grown to38. States are also working to prevent further contamination by banning or phasing out MTBE use, sampling drinking water wells, funding studies on MTBE cleanup, investigating alternatives to MTBE, and calling for EPA to move quickly to set a maximum contaminant level (MCL) for MTBE.

U.S. Environmental Protection Agency (EPA) statistics indicate that over 1,459,627 million petroleum underground storage tanks (USTs) have been closed nationwide since the UST program was created in 1988, leaving about 713,666 regulated USTs currently in service. Unfortunately, many of these tanks are known to have leaked, contaminating soil and ground water. EPA estimates that, as of September, 2000, there are currently over 412,392 confirmed releases or leaking underground storage tanks (LUSTs) in the U.S. There are about 367,603 cleanups initiated with 249,759 cleanups completed to date, leaving about 162,633 open LUST cases (*1*).

Until recently the chemical of greatest concern at these LUST sites was benzene, a naturally occurring hydrocarbon refined from crude oil, found at all gasoline release sites. Benzene content in gasoline is typically 1% or less by volume, with historic levels as high as 4% by volume. Benzene is a known human carcinogen, and even low level exposures are considered unacceptable. The federal maximum contaminant level (MCL) is 5 parts per billion (ppb). However, considering the large numbers of LUSTs, and the number of years that benzene has been in use, drinking water impacts have been minimal. This is because, when benzene is released it tends to dissolve slowly and migrate relatively slowly in ground water. Benzene also biodegrades quickly. Due to low concentration in the fuel source, slower migration and rapid biodegradation, dissolved benzene plumes tend to attenuate over relatively short distances, reducing the possibility of migration to potential receptors.

Methyl tertiary butyl ether (MTBE) was added to gasoline as early as the 1970's at levels up to 7% by volume to increase octane of unleaded fuels. More recently MTBE has been added to gasoline at levels 11% to 15% by volume to comply with the 1990 Clean Air Act requirements for increased oxygen content as part of the Federal reformulated gasoline (RFG) and Wintertime Oxyfuel programs initiated by EPA in 1995 and 1992, respectively (*2*). These programs are intended to reduce automobile tailpipe emissions in U.S. cities with the worst air pollution. The clean air act stipulates that by 1995, RFG must provide a 15% reduction in air toxics emissions over 1990 gasoline. By 2000, RFG must provide a 20% reduction in air toxics emissions. EPA Office of Mobile Sources reports that emission reductions from the RFG program have been more than the program requires each year since the program's introduction (*3*).

Because MTBE has only recently been added to gasoline in high volumes, it is not found at all gasoline release sites. However, Lawrence Livermore

National Laboratory recently estimated that there are greater than 10,000 LUST sites impacted by MTBE in California alone (4), and MTBE has been detected at LUST sites in almost every state (5). When released, MTBE tends to dissolve quickly, relative to other constituents of gasoline. Once dissolved MTBE tends to stay in the water and migrate at the rate of ground water flow, due to a low Henry's law constant and a low organic carbon partitioning coefficient. In addition, MTBE does not degrade or break down as quickly as benzene. As a result, dissolved MTBE plumes are expected to migrate faster and attenuate over longer distances than benzene plumes (6). The toxicity of MTBE is currently being debated, U.S. EPA has set a consumer acceptability advisory level of 20-40 ppb (7). However, The physical and chemical properties of MTBE, along with the relatively high concentration in the gasoline source, increase the possibility for migration to potential receptors

Development of State Cleanup Standards for MTBE

Federal EPA has delegated responsibility for the UST program to the states. State requirements must be no less stringent than the federal requirements (8). As a result, many state programs use the federal MCLs as cleanup or action levels for contaminants in soil and ground water. However, in the absence of a federal MCL for MTBE the states have developed their own varied approaches to regulating MTBE.

In November 1993, EPA's Office of Research and Development published a report titled "Assessment of Potential Health Risks of Gasoline Oxygenated with Methyl Tertiary Butyl Ether (9)." This report stated "there is no reason, to say there is a serious carcinogenicity public health hazard from the inhalation of MTBE, although some hazard is possible and necessarily should be further evaluated." This report also speculated that carcinogenicity of the "MTBE component itself seems to be no worse than the non-oxygenated gasoline mixture." Toxicological concern for MTBE's carcinogenicity focused on inhalation risk, and was not particularly related to the risks associated with drinking MTBE-contaminated ground water. In the early 1990's and up to late 1996, only a few states had even a limited understanding of the distribution and occurrence of MTBE contamination in ground.

As additional data became available from the U.S. Geological Survey in October 1996, the widespread occurrence of MTBE was noted in shallow

ground water, and, to a lesser extent, in deeper ground water (10). The USGS study offered the first comprehensive nationwide "glimpse" of MTBE occurrence and distribution. Based on monitoring data collected by the USGS, it appeared that wells most susceptible to contamination were shallow ground water wells in urban areas. The most obvious source of MTBE contamination in shallow ground water were LUST sites that spilled or released gasoline containing MTBE, although other point and non-point sources were also implicated by the USGS data.

However, most state UST/LUST regulatory programs were not able to quickly connect the USGS work to their state-specific LUST sites. States' reactions in 1997 to increasing evidence of ground water contamination by MTBE varied from believing that existing programs would be sufficient to address this contaminant, to vigorous state actions in developing new guidance or regulations to address MTBE cleanup. A few states initiated ground water sampling programs, primarily at or near LUST sites, to assess the state-specific occurrence and distribution.

During the middle of 1997, all 50 state and District of Columbia UST/LUST regulatory programs were contacted through phone interviews to assess MTBE ground water cleanup requirements. The interviews were intended to better understand the individual state's approach to regulating MTBE contamination in ground water. The information collected from these initial interviews indicated that 18 states had specified levels for MTBE, either as guidance or specified cleanup values. Cleanup levels ranged from 12 ppb (Wisconsin) to 230 ppb (Michigan). At least three states indicated "site-specific" considerations were available within their UST/LUST program to set MTBE cleanup levels as needed. In 1997, the majority of the states were expecting a MCL to be established by the EPA, thus eliminating the need for states to enact their own MCL for MTBE (Figure 1).

For the most part, in September 1997 state-specified MTBE cleanup and drinking water levels were at, or below, the upper concentration range (200 ppb) given in the U.S. EPA's draft 1992 MTBE Drinking Water Health Advisory (11). However, this 1992 draft Health Advisory also specified 20 ppb as the lower value of the concentration range based on uncertainty regarding the carcinogenic potential of MTBE. In December 1996, the U.S. EPA released a new draft Lifetime Health Advisory for MTBE at 70 ppb to replace the 20-200 ppb range set in 1992 (12).

The MTBE issue is further complicated by apparent aesthetic qualities of taste and odor associated with MTBE-impacted drinking water supplies. EPA
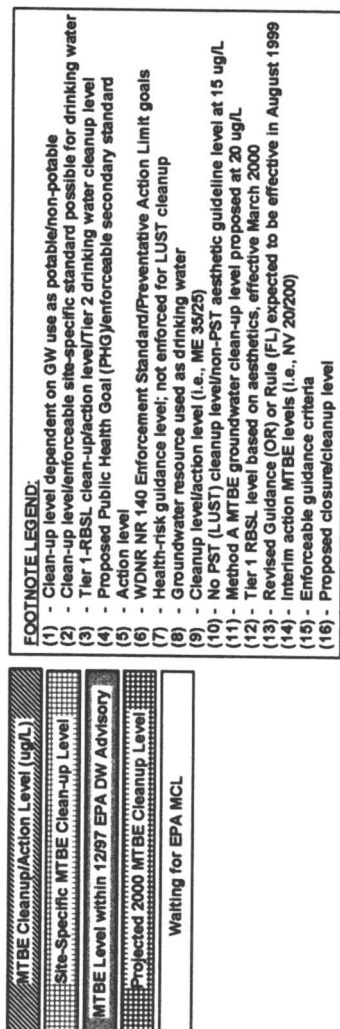
Figure 1. MTBE Groundwater cleanup levels for LUST sites, current and proposed as of September, 1997. Based on telephone interviews with state UST/LUST program personnel. (Reproduced with permission, Copyright 2000 Delta Environmental Consultants, Inc.)

addressed these issues with its December 1997 "Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (7)." This advisory acknowledged that "MTBE is generally unpleasant in taste and odor" in drinking water. EPA's Advisory also noted that the degree of human health risk from MTBE toxicity due to ingestion of low-level MTBE contamination in drinking water could not be accurately determined from the MTBE toxicity database that was available in 1997. Finally, the Advisory recommended "that keeping levels of MTBE contamination in the range of 20 to 40 ug/L [ug/L $\cong$ ppb] or below to protect consumer acceptance of the water resource would also provide a large margin of exposure (safety) from toxic effects."

During 1998-1999, the status of state-specific UST/LUST regulatory requirements for MTBE ground water cleanup were periodically updated using phone interviews. These results of these phone interviews indicated increasing concerns over MTBE contamination in drinking water and ground water from releases and spills at LUST sites. In February 2000, 21 states had, or projected having, MTBE ground water cleanup levels within or below the December 1997 EPA Advisory range (20 to 40 ppb). In addition, 13 states had MTBE cleanup levels above the Advisory range and 4 other states maintained "site-specific" ability to apply MTBE cleanup levels. Only 12 states did not have MTBE cleanup levels for contaminated ground water. . The majority of the states without established MTBE cleanup or action levels were still expecting an EPA MCL to be established that would preclude the need for a state-specific MCL initiative (Figure 2).

MTBE notoriety and public awareness increased in January 2000 with "60 Minutes" CBS news story (13) on the nationwide occurrence of MTBE ground water contamination and drinking water impacts. In the same month, EPA's Office of Underground Storage Tanks (OUST) issued a memorandum to regional and state UST/LUST programs that strongly recommended monitoring and reporting of MTBE and other oxygenates at UST release sites (14). The same memorandum encouraged adequate MTBE investigation and remediation to minimize impacts to drinking water supplies resulting from ground water contamination at UST/LUST sites.

In summary, the late 1990's noted a changing awareness by regulators and the public regarding MTBE's occurrence and distribution in the nation's ground water. Given the EPA Office of Water's estimation that promulgating a MCL for MTBE would require 6 to 10 years, once the process is initiated, EPA and states have been forced to reevaluate their response to the MTBE issue   In the

MTBE Cleanup/Action Level (ug/L)

Site-Specific MTBE Clean-up Level

MTBE Level within 12/97 EPA DW Advisory

Projected 2000 MTBE Cleanup Level

Waiting for EPA MCL

FOOTNOTE LEGEND:
(1) - Clean-up level dependent on GW use as potable/non-potable
(2) - Clean-up level/enforceable site-specific standard possible for drinking water
(3) - Tier 1-RBSL clean-up/action level/Tier 2 drinking water cleanup level
(4) - Proposed Public Health Goal (PHG)/enforceable secondary standard
(5) - Action level
(6) - WDNR NR 140 Enforcement Standard/Preventative Action Limit goals
(7) - Health-risk guidance level; not enforced for LUST cleanup
(8) - Groundwater resource used as drinking water
(9) - Cleanup level/action level (i.e., ME 35/25)
(10) - No PST (LUST) cleanup level/non-PST aesthetic guideline level at 15 ug/L
(11) - Method A MTBE groundwater clean-up level proposed at 20 ug/L
(12) - Tier 1 RBSL level based on aesthetics, effective March 2000
(13) - Revised Guidance (OR) or Rule (FL) expected to be effective in August 1999
(14) - Interim action MTBE levels (i.e., NV 20/200)
(15) - Enforceable guidance criteria
(16) - Proposed closure/cleanup level

Figure 2. MTBE Groundwater cleanup levels for LUST sites, current and proposed as of February, 2000. Based on telephone interviews with state UST/LUST program personnel. (Reproduced with permission, Copyright 2000 Delta Environmental Consultants, Inc.)

near term, the majority of actions to minimize and eliminate existing MTBE contamination are being undertaken by the states rather than the federal government. Some states have already acted to phase out or eliminate the use of MTBE as an oxygenate in gasoline distributed within their state. State UST/LUST programs also realize the need for frequent communication with their respective state drinking water programs in working more effectively together to prevent future, and solve existing MTBE contamination problems.

State UST/LUST Program Responses to MTBE Contamination

State UST/LUST programs are concerned about the widespread impacts of MTBE. The most poignant and pressing question is "what level of MTBE contamination is acceptable or safe in drinking water?" Until additional toxicological data is collected this question cannot be completely answered. In addition, the testing of public water supply wells takes time. Many states are reluctant to conduct statewide testing for a compound for which no federal MCL exists. Even worse, many shallow, private wells are not tested on a regular basis and may be at greater risk. Though most states have established cleanup and action levels for MTBE, phone survey results indicate that many states still want EPA to complete the human health studies that will lead up to the establishment of a federal MCL for MTBE to support state standards.

However, this does not mean that state UST/LUST programs are not addressing MTBE issues. In fact, states have recognized the need to proactively manage MTBE impacted sites and prevent the migration of new gasoline releases that contain MTBE. States are calling on EPA to enhance communication between the Offices of Underground Storage Tanks, Air (Office of Mobile Sources), Drinking Water, Ground Water, and Office of Research and Development so that future decisions on reformulation of gasoline consider all of the consequences of any changes in fuel chemistry. A number of states have been forced to close drinking water wells impacted by MTBE and have begun aggressive remediation programs. Some state weights and measures departments are now routinely testing for oxygen concentration in gasoline to determine if MTBE is present in the state's fuel supply. States are seeking funding for innovative technology pilot remediation programs Many states are mapping UST/LUST locations on GIS overlays that will allow for a more integrated analysis of aquifer vulnerability.

To enhance communication on MTBE issues the Association of State and Territorial Solid Waste Management Officials (ASTSWMO) created a fuel

oxygenate workgroup. The workgroup includes State and EPA LUST regulatory personnel, the US Geological Survey, the American Petroleum Institute (API), environmental consulting firms and municipal water suppliers. ASTSWMO publishes a newsletter to make information on MTBE issues available to as many state regulators as possible (*15*). The remainder of this section provides information on some of the specific actions being undertaken by selected state programs to illustrate the variety of actions being taken nationwide with respect to MTBE. Many other states have ongoing activities that were not possible to include in the space available. This information was contributed to the ASTSWMO oxygenate workgroup by state agency participants.

Arizona

The State of Arizona published a report on MTBE in October 1999 (*16*). The report recommended that Arizona consider EPA decisions on the future use of MTBE, it recommended that Arizona compile information on MTBE impacts to surface water and groundwater, and compile information on active UST system compliance with UST regulations. A statewide groundwater study is in the planning stages, which will assess aquifer vulnerability to fuel releases.

California

In California an estimated 78% of Leaking Underground Fuel Tank (LUFT) sites are impacted with MTBE (*4*). Testing of public water supply wells indicates that 40 public water supply wells currently contain detectable concentrations of MTBE. As a result of these widespread well impacts and the state's determination of MTBE as a carcinogen, California has proposed a primary state MCL for drinking water of 13 micrograms per liter (ug/l) and a secondary state MCL of 5 ug/l. In 1999 Governor Davis ordered a phase-out of MTBE from all fuels in California by no later than December 31, 2002 (*17*). This report lays out 11 tasks to support the ban on MTBE in California including labeling of gasoline containing oxygenates, extending the life of the LUST cleanup fund, funding a study by Lawrence Livermore National Laboratory to evaluate ethanol as a replacement for MTBE (*18*), and creating guidance on assessment and remediation for MTBE (*19*). To address concerns over cases that have been previously closed, the state has issued guidance for re-evaluating closed LUFT cases for possible MTBE impacts (*20*). California

also recognized the impact of MTBE on surface waters by banning the use of two-stroke engines on reservoirs which store water for drinking water purposes.

Hawaii

The State of Hawaii completed a refinery survey in 1998 to determine the history of the use of MTBE (21). Hawaii found that MTBE had been used in local refineries and imported from the mainland as recently as 1997. As a result of these findings and based on reports of MTBE impacts from the mainland, Hawaii established Tier 1 RBCA cleanup standards for MTBE in ground water of 20 ppb in areas where drinking water is threatened and 202,000 ppb in areas where drinking water is not threatened.

Kansas

In Kansas, the Department of Health and the Environment (KDHE) implemented an MTBE action level of 20 ug/l for impacted drinking water wells. However, all public or domestic supply systems will be assessed and reviewed at any detectable level. A rigorous well testing program of all 1,122 public water systems found that 18 systems (30 wells) were impacted with MTBE. Average flow rates of the supply wells range from 225-1,000 gallons per minute. Kansas has implemented a risk-based approach for prioritizing cleanups at MTBE contaminated sites based upon the potential for the plume to impact currently used drinking water. MTBE treatment systems are in operation at three of the more heavily impacted public water supply systems. The potable water treatment systems are capable of achieving MTBE reductions between 94% and 100% (22). There are three additional treatment systems in design phase.

MTBE remediation systems are operating at over 100 of the most severely impacted sites that are in proximity of a drinking water receptor. Another 100 in situ remediation systems are in either design or installation phase. Many of these systems should be operational within the next year. Initial results indicate that MTBE can be remediated with conventional in situ LUST remedial technologies. Several in situ remediation systems in Kansas have achieved an MTBE reduction of up to 100% (22). The state has also instituted a program that provides strong incentives for environmental consultants to keep remediation systems operational and optimized. Kansas is also considering

legislation to ban MTBE and impose penalties for sale of gasoline containing MTBE.

Maine

Maine established a 5 ug/l notification level for MTBE and a 15 ug/l level triggering cleanup. Five public water supply systems (PWS) are currently known to be impacted with MTBE. Maine requires treatment of drinking water containing 13 ug/l or greater MTBE. There are 220,000 private wells in the State of Maine. Many of these wells are shallow wells completed in bedrock aquifers that are vulnerable to MTBE contamination. Maine identified this problem through a state mandated study which surveyed 950 private domestic drinking water wells (23). The study found that 15.8 % of the domestic wells were impacted with MTBE. House Joint Resolution (HJR) 9 seeks to eliminate the oxygenate requirement in the State of Maine. In October, 1998, Maine published a Five Point Plan for addressing MTBE issues that include testing of water wells, evaluating alternatives to MTBE, creating a wellhead protection initiative, creating of a workgroup to improve communication between state agencies, and creating a waste gasoline disposal program (24).

Maryland

Maryland has also been widely impacted with MTBE. The Baltimore and Washington, D.C. metro areas are part of the RFG Program. Based on 1995-2000 data, MTBE was detected in 66 of 1,060 public water supply systems, 10 of which contained concentrations of MTBE >20 ug/l (8 of which have alternate sources). LUST site data indicates that 210 private domestic wells have been impacted with MTBE. No surface water supplies have been impacted to date. Maryland has a site-specific cleanup level for MTBE and a 20 ug/l action level for MTBE in drinking water.

Montana

Montana uses MTBE for octane purposes only. There are no RFG areas in Montana. However, the Missoula area is part of the winter oxyfuels program and used MTBE during the winter of 1992 until citizen complaints prompted the county health department to convince local petroleum suppliers to use ethanol. Montana's groundwater cleanup standard is 30 ug/l. The Montana

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DEQ estimates that 30-50 % of its LUST sites are impacted with MTBE. One large release site in northwest Montana has a 2,000 feet long MTBE plume. Public water supply wells were not tested for MTBE prior to 1999 so little information is available on the impact of MTBE to the state's drinking water wells.

New Hampshire

The State of New Hampshire has found that 100% of its LUST sites are impacted with MTBE. Statewide testing of public water supply wells indicates that 215 (18.7%) of 1,150 PWS wells are contaminated with MTBE. New Hampshire has proposed a Primary Drinking Water standard of 13 ug/l and a Secondary Drinking Water standard of 20 ug/l. The current drinking water and groundwater cleanup standard is 70 ug/l. New Hampshire's data indicates that neighboring states are likely affected by MTBE releases that are migrating out of the state and across the borders.

Wisconsin

In Wisconsin, MTBE usage is highest in the City of Milwaukee and surrounding counties that are part of the winter oxyfuels program. Although ethanol is widely used in Wisconsin, due to the proximity of ethanol production plants, Wisconsin estimates that over 50% of its LUST sites are impacted with MTBE. One plume, located in the town of Spring Green, has a 4,500 feet long plume that has impacted the town's water supply well. The state's MTBE groundwater cleanup standard is 60 ug/l. Wisconsin is considering increasing its ethanol production and use as a result of the widespread impacts of MTBE.

Conclusions

MTBE was added to gasoline to solve air quality issues and to provide octane enhancement during the lead phase out but resulted in unexpected impacts on soil and water. Today UST and drinking water programs are scrambling to find solutions to address these impacts. In 1997 18 states had cleanup or action levels for MTBE. In 2000, the number of states with cleanup or action levels for MTBE had grown to 38. In addition, states have moved to proactively manage MTBE impacts and prevent further contamination of ground water by banning or phasing out MTBE use, working to improve

communication between air and drinking water programs, sampling drinking water wells, funding studies on MTBE cleanup, investigating alternatives to MTBE, and calling for EPA to move quickly to set a MCL.

This situation points out the need to carefully consider potential environmental consequences when selecting and formulating chemicals. This is especially important for those chemicals that will be used widely and stored in USTs across the country. We should consider potential impacts over the entire life cycle of chemical production, storage, transport and use. Environmental mobility and attenuation rates should also be carefully examined when selecting chemicals for widespread use. The MTBE problem illustrates how fuel composition decisions can have profound environmental and policy impacts.

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Chapter 5

Use and Occurrence of Fuel Oxygenates in Europe

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In contrast to the US, fuel oxygenates are generally used as octane enhancers in Europe rather than to increase the oxygen level in gasoline for a cleaner combustion. To achieve the high average octane ratings of European gasolines (95 RON), currently more than 2.5 Mt/a of fuel oxygenates, mainly methyl tert-butyl ether (MTBE) are used. Stimulated by the public discussion in the US, there is a growing awareness of groundwater pollution related to the use of MTBE as a gasoline component. Although the number of leakage and spill sites in Europe is supposedly lower than in the US due to earlier implementation of strict storage facility regulations, contamination of groundwater with MTBE is significant. Owing to the lack of a uniform European standard, however, the situation may vary considerably in

different European countries. Recent survey studies in northern and central Europe on groundwater pollution by MTBE revealed background concentrations of up to 3 µg/L, and concentrations at point sources of up to 500 mg/L. For southern and eastern European countries there is no data available to us on regulations or MTBE levels in the environment. Due to growing concern regarding groundwater pollution by MTBE, alternative octane enhancers are put forward in some European countries. While the dialkyl ethers tert-amyl methyl ether (TAME) and ethyl tert-butyl ether (ETBE) are already in use, the introduction of ethanol is being discussed.

Introduction

Methyl tert-butyl ether (MTBE) and more recently other fuel oxygenates such as ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME) are used in substantial amounts in Europe. Unlike in the US, there has been hardly any public discussion on the use of fuel oxygenates in Europe to date. Reasons for this include

(a) the less pronounced use compared to oxyfuel (oxygenated fuel) or RFG (reformulated gasoline) areas in the US;
(b) an earlier awareness of fuel storage facilities as a potential environmental problem in some European countries
(c) most drinking water supplies in Europe do not depend on shallow groundwater which appears to be particularly threatened by MTBE contamination.

While a phase-out of MTBE in gasoline finds increasing support throughout the US, the German Environment Agency (UBA) recently recommended an increase in the use of MTBE, in order to further reduce the content of benzene and other aromatics in gasoline (1). In contrast, environmental agencies in Denmark, the Netherlands, Switzerland and the U.K. have initiated national studies to investigate environmental problems arising from intense MTBE use, and the Finnish Environment Institute carries out an MTBE risk assessment for the European Union (2). At the same time, an independent risk assessment is in progress at CEFIC, the European organization of chemical manufacturers (3). It is expected that both

assessments will identify the most important areas for further research in Europe.

Up to now only little is known about the use and environmental occurrence of fuel oxygenates outside the US. This is partly due to the fact that hardly any study presenting European data has been published in the reviewed literature. The objective of this chapter is therefore to provide an overview of the European situation regarding the consumption of fuel oxygenates, pertinent regulations and preliminary studies of MTBE occurrence in ground- and surface water.

Throughout the text the term EU is used to address specifically the 15 member states of the European Union. Otherwise, we use the term Europe.

Fuel oxygenate regulation and consumption

Table I summarizes the EU legislation for gasoline from 1985 to 2005 and compares it to current US regulations. In 2000 and 2005, new EU regulations for gasoline will come into effect, restricting the content of overall aromatics and benzene in particular in several stages. Furthermore, since January 1, 2000 the use of alkyl lead compounds as octane enhancers is prohibited. To maintain the required research octane number of 95 for the most commonly sold premium grade gasoline, a high octane substitute has to be added, which in turn is expected to result in an increase in the fuel oxygenate consumption. Present EU regulations on the content of different oxygenates in gasoline are shown in Figure 1. In European directives there are no minimum oxygen requirements but some countries (e.g. Finland) require oxygenate contents similar to the US for special grades of gasoline.

MTBE production in Europe began in 1973 (first commercial plant in Italy) but in the seventies MTBE was used only on a modest scale as an octane enhancer. With the decline of alkyl lead consumption during the eighties, the use of MTBE as an octane replacement increased very quickly. In the nineties, MTBE use in Europe was stable or even decreased slowly due to more experience in refining and less consumption of premium gasoline (10). There are no official statistics on the use of MTBE in European countries available to us, which makes it difficult to quantify MTBE consumption accurately over the past two decades.

Table II gives an overview of gasoline and MTBE consumption in individual European countries. The current amount of MTBE used in Europe will be higher than the 2.2 Mt/a reported in Table II because:

(a) Several countries are missing in the statistics (eastern European countries, Ireland, Luxembourg);

(b) New EU directives have become effective 01/01/00 (e.g. ban of leaded gasoline, restrictions of benzene and aromatics content).

Table I. Maximum concentrations of gasoline compounds in EU and US regulations (revised from (4)).

effective	EU 1985	EU 1995	EU 2000	EU 2005	USA RFG[a]	USA CA2RFG[b]	USA after phase out of MTBE
Aromatics, % v/v		-	42	35	25	30	
Benzene, % v/v		5	1	1	1	1.2	
Oxygen content, % m/m	2.5 or 3.7	2.5 or 3.7	2.7	2.7	min: 2.7 max: 3.5	min: 1.8[c] max: 2.7	no min. requirement?
Ethers containing 5 or more carbon atoms per molecule, % v/v	10 or 15	10 or 15	15	15			
Sulfur content, mg/kg		500	150	50		80	
Lead content, g/l		0.013	0.005	0.005		0.013	
Reference	(5)	(6)	(7)	(7)	(8)	(8)	(9)

(a): Absolute limits (cap) for US federal reformulated gasoline (RFG) for all states except for California

(b): Absolute limits (cap) California Phase 2 reformulated gasoline (RFG)

(c): No minimum oxygen required in summer
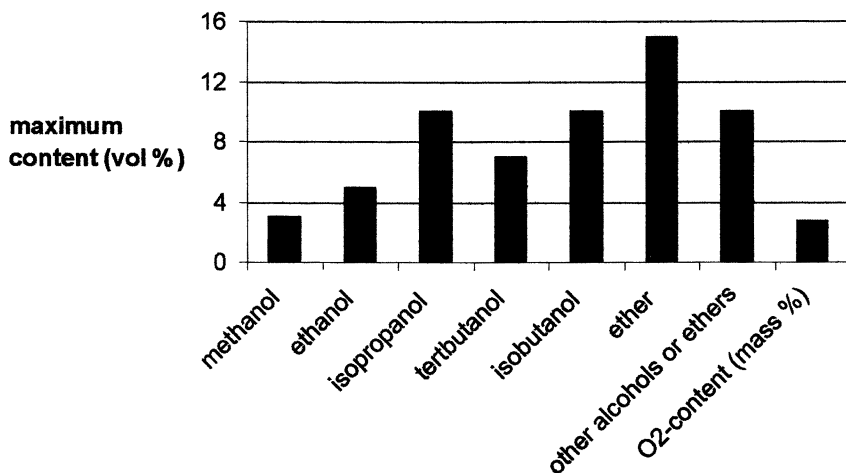
Figure 1.   *Oxygenate regulation in Europe (7)*

The MTBE consumption is expected to increase to 3.8 Mt/a over the next 5 years (*11*).

In 1997 there were 25 MTBE-producing companies in the EU with 35 operating facilities. The average percentage of MTBE in the gasoline pool in Europe is about 2 vol %, ranging from 0.2 to 3.9 % for individual countries. Finland has an exceptionally high average MTBE content in gasoline of about 9 %.

In addition to MTBE, about 0.1 Mt/a of TAME are used as a fuel oxygenate in Finland (*1*). In France, Italy and Spain, the consumption of ETBE will probably increase even more rapidly than the use of MTBE due to tax incentives for the use of ethanol which is used to produce ETBE (*3*). In 1998, the use of ETBE was already significant in France with about 0.16 Mt/a (*12*) and Italy (no reliable data available). In the past, the use of tert-butyl alcohol (TBA) and methanol in Germany amounted to more than 0.03 Mt/a but nowadays alcohols are rarely used as fuel oxygenates in Europe.

In conclusion, there are some major differences in the gasoline and fuel oxygenate markets of the US and Europe. In Europe, fuel oxygenates are added to increase the octane rating of the fuel rather than to reduce emissions from vehicles as it is done in the US. Consequently, the oxygenate levels in gasoline are lower in Europe but also more uniform than in the US (with the exception of Finland). MTBE is by far the most common fuel oxygenate in Europe today. In contrast to the US, ethanol is not (yet) widely used as a fuel oxygenate, while TAME and ETBE are used in substantial amounts.

Table II. **Average consumption of gasoline and MTBE in Europe in 1996/97**

Country	Grade (RON)	Number of samples	estimated gasoline sales in million tons/a	MTBE content in vol. %	amount MTBE in 1000 t/a
EU-members:					
Austria	91	10	0.744	0.9	6.7
	95	10	1.108	3.7	41.0
	98	10	0.352	8.3	29.2
Belgium	95	9	1.005	0.1	1.0
	98	9	1.022	2.5	25.6
	98L	8	0.712	1.2	8.5
Denmark	92	4	0.228	0	0.0
	95	18	0.794	0.4	3.2
	98	14	0.888	6.3	55.9
Finland	95	7	1.291	8	103.3
	98	5	0.27	12.4	33.5
	99	0	0.27	nd	
France [a]	95	20	2.159	nd	200.0
	98	20	6.23	nd	
	SL	0	6.609	nd	
Germany	91	96	11.291	0.3	33.9
	95	96	16.342	1.6	261.5
	98	80	1.6	6.2	99.2

Table II. *Continued.*

Country	Grade (RON)	Number of samples	estimated gasoline sales in million tons/a	MTBE content in vol. %	amount MTBE in 1000 t/a
Greece	95	27	1.104	3.5	38.6
	98	3	0.085	8	6.8
	96L	37	1.818	0.2	3.6
Italy	95	62	7.932	4.3	341.1
	97L	62	9.742	1.9	185.1
Netherlands	95	8	3.145	0.8	25.2
	98	8	0.711	5.4	38.4
	SL	8	0.335	1.2	4.0
Portugal [a]	95	0	0.447	nd	50.0
	98	0	0.355	nd	
	SL	0	1.143	nd	
Spain	95	8	1.809	4.7	85.0
	98	5	1.266	8.5	107.6
	97L	8	5.97	2	119.4
Sweden	95	47	3.146	0.3	9.4
	98	34	1.116	6	67.0
United Kingdom	95	11	14.522	0.1	14.5
	98	8	0.709	0.21	1.5
	SL	11	7.178	0.1	7.2

Non-EU members: [b]

Hungary	91	0	0.215	nd	11.8
	95	15	0.59	2	2.9
	98	4	0.03	9.5	
	92L	0	0.114	nd	
	98L	15	0.322	1.1	3.5
Norway	95	22	1.135	3.8	43.1
	98	20	0.226	5.1	11.5
	SL	0	0.362	nd	
Switzerland [c]	95	20	3.256	2.5	81.5
	98	17	0.21	10.4	21.6
	SL	0	0.36	nd	
Sum EU members:			**115.5**		**2007**
Sum Non-EU members:			**6.82**		**176**

[b]

nd: not determined

L: leaded gasoline (share decreasing)

RON: Research Octane Number

SL: super leaded (no RON specified)

(a):   MTBE consumption data for France and Portugal are from (13)

(b):   Data available only for few countries

(c):   The share of premium gasoline (98 RON) in Switzerland was estimated to be 6 % (14)

Storage facilities

Leaking pipelines and underground storage tanks (USTs) are the major point sources of groundwater contamination with gasoline (*15*). Not only leaking tanks but also emissions during transport and storage of gasolines, i.e., piping, pumping, filling of the tank, and refueling of vehicles, are to be considered (*16*). In fact, many incidents of gasoline contamination of groundwater occurred not due to leaks in storage tanks but during other stages in the chain of gasoline distribution (mainly leaks in the piping). For many of these stages during gasoline transport and storage, there are individual regulations and various responsible authorities. In the US, nearly 100 codes apply to underground storage management and operation (*16*). In Europe, the number of regulations is of the same order of magnitude. This large number of regulations makes the comparison of regulations in different countries very difficult.

There are no general European regulations for underground storage tanks. Currently, an EU guideline is under preparation for large USTs (> 5,000 tons) whereas smaller USTs will continue to be regulated on a national or regional level. National regulations in European countries are based on two different philosophies:

(a) Risk based regulations (e.g., in the United Kingdom) where requirements for storage tanks are set locally based on the degree of water protection required and

(b) Generic specifications of tank features (e.g., Germany) where the requirements for the construction and operation of underground storage tanks are independent of location (*17*).

In addition, generic specifications can also be combined with certain risk based requirements. For example, in Germany, priority water pollutants must not be stored or even transported in designated water protection areas. Gasoline is classified as a priority pollutant based on the toxicity of the aromatics. MTBE alone is categorized as a low risk chemical, regardless of the fact that in cases of leaking USTs MTBE is the most mobile and recalcitrant gasoline-derived pollutant of groundwater.

Basic regulations for the construction and operation of underground storage (double wall tanks, leak detection systems, spill containment) are similar for Denmark, Germany, the United Kingdom, Switzerland and the US. However, implementation of these regulations began earlier in these European countries than in the US. Furthermore, the scope of regulations differs among countries. "Small" tanks are generally excluded from the stringent regulations but "small" may be defined as <20 liters in Switzerland or <5,000 liters for residential tanks in the United States. Thus, even though major specifications

for the construction may be quite similar, the scope of the regulations may differ significantly. Based on recommendations of the blue ribbon panel the limited scope of storage tank regulations is currently being reviewed by the US EPA (9): "In the future, the universe of regulations may be expanded to underground and aboveground fuel storage systems that are not currently regulated but yet pose substantial risk to drinking water supplies". There is no information about regulations in other European countries available to us but we assume the standards are often lower.

It must be emphasized that new installations do not ensure leak prevention. In a recent Californian study, leakages at 1998-upgrade-compliant UST systems were reported (18). One reason might be that leak detection systems are not able to detect small, subtle losses of gasoline. These leaks can still lead to pollution of water resources and are considered the "primary challenge" in UST operation today (16).

Regulations of technical devices alone are not adequate to improve the quality of underground storage facilities since the quality of both installation and operation is also of major importance. Improper UST system installation has been identified as one of the primary causes of fuel releases to the environment (16). Operators of tank facilities must be educated to enable them to use equipment appropriately and to identify problems and possible leaks as early as possible. In Germany for example, there are strict regulations on the qualifications required for installing and maintaining an UST (e.g., (19)). Personnel qualification and general awareness differ between the US and Europe and among individual European countries.

To evaluate the effect of all measures taken to protect groundwater from gasoline contamination, performance studies are required. Results from such studies can help evaluate whether strict regulations and highly trained personnel really do result in the desired effects and subsequently to direct future resources to improve water quality. In the US, a number of studies on UST safety were performed and a comprehensive summary is compiled in (16). The suggestions of the blue ribbon panel for improving current practice are mostly the result of analyzing UST performance data (9). To the knowledge of the authors no such studies have been published for Europe.

Environmental and drinking water regulations

The European Union has almost completed an environmental and health risk assessment for MTBE led by Finnish authorities (2). The draft report of November 2000 contains an extensive section on exposure assessment. It is estimated that up to 50 % of the European population may be exposed to low

levels of MTBE (about 0.1 µg/L) in drinking water resulting from diffuse contamination sources, and 0.1-1 % to perceptible MTBE levels (more than 15 µg/L) resulting from point source contamination.

The World Health Organization (20) recently concluded that under common exposure conditions it appears unlikely that MTBE induces adverse acute health effects in the general population. However, due to the low odor and taste threshold values of MTBE, water may be spoiled for drinking water purposes even before toxic levels are exceeded. To date, there are no regulations for MTBE in water, air or soil in Europe. Guideline values based on toxicity and malodorousness of MTBE were published in Denmark (21) which are summarized in Table III. These values are similar to threshold values used throughout the US. A recent investigation by the Danish EPA resulted in lower odor and taste limits (7 µg/L) than previously reported and thus may be used to justify lower threshold values in the future (22).

In Switzerland, a guideline value for MTBE in groundwater of 2 µg/L is discussed (25). If exceeded, measures to abate pollution are recommended but are not enforceable. This low value was chosen based on the precautionary principle, using MTBE as a tracer for gasoline contamination of groundwater. The preference for precautionary based guidelines or threshold values (as for pesticides in drinking water) is one of the distinct differences between European and US legislation, since in the US a risk-based approach for each individual compound is preferred.

Occurrence in aqueous systems

Fuel oxygenates may contaminate groundwater reservoirs in the vicinity of point sources due to accidental spills, overflows or leakages. Potential non-point or diffuse sources of fuel oxygenates are urban or street runoff and precipitation which recharge groundwater reservoirs. Surface water bodies can be additionally affected by motorboating activities as a large amount of unburned gasoline is released from watercrafts, especially from 2-stroke engines (26). On the other hand, MTBE in surface water may volatilize quite rapidly, depending on wind speed, flow depth and velocity (27).

Squillace et al. (28) give an overview on the occurrence and possible sources of MTBE in shallow groundwater samples in the US. In this study, high concentrations of MTBE are attributed to point sources, and low concentrations frequently found in shallow urban groundwater to non-point sources. A similar study of source attribution in Europe has not been carried out to date. Most investigations so far report on MTBE, very few included TBA, the major degradation product of MTBE in aqueous sytems. Data for other fuel oxygenates are not available.

Table III. Comparison of suggested maximum target concentrations for MTBE in different environmental media for Denmark and the US (revised from (3)).

Country	Air	Soil	Water	Reference
Denmark [a]	0.26 mg/m^3 (toxicity) 0.03 mg/m^3 (odor)	500 mg/kg (toxicity) 0.3 mg/kg (odor)	350 µg/L (toxicity) 30 µg/L (odor)	(21)
US	not available	0.2 - 3300 mg/kg [b]	20 - 510 µg/L [b] 20 - 40 µg/L [c] 5, 13 µg/L [d]	(15, 23, 24)

(a): The two given concentrations are either based on toxicity or on odor

(b): Overall range for different states. For soil: range of cleanup levels, for water: drinking water standards

(c): US EPA drinking water advisory on consumer acceptability and health effects analysis

(d): California department of health services secondary and primary drinking water limit.

Diffuse input and background concentrations

Few regional or national studies for MTBE were done in the last few years, results of which are summarized in Table IV (groundwater) and Table V (surface water). So far, a systematic monitoring of water samples for fuel oxygenates has not been carried out in Europe.

In a survey from 1999 in Germany, 180 groundwater samples were investigated. 90 groundwater samples were from rural areas and 90 from urban areas. MTBE was detected (conc. > 50 ng/L) in 9 % of the samples taken from rural areas, whereas in urban areas more than 53% were MTBE positive, 28 % of which contained more than 0.5 µg/L. The contamination potential of MTBE for groundwater in urban areas therefore appears to be significantly higher than in rural areas.

In the United Kingdom, a number of regional water boards and water companies carried out investigations, yielding the most extensive dataset in Europe. However, it is not possible to separate monitoring data from data for boreholes affected by known incidents. The UK numbers in Table IV may therefore be biased towards a higher percentage of reported positives.

In ground and drinking water samples from Switzerland and Denmark without obvious influence of point sources, MTBE was found frequently at low concentrations (highest level 0.8 µg/L, mostly less than 0.5 µg/L). In Kanton Zuerich, Switzerland, monitoring of 100 groundwater wells for MTBE (and other VOC) began in 1996. This is the only case so far where data from the same wells over a longer time period is available (see Figure 2). Within just a few years, the number of positive MTBE findings increased from 0 to 25 %. Samples containing MTBE were found in different groundwater supplies and even in a deep aquifer supposedly protected by an overlying aquitard and aquifer.

In 1999, MTBE was the most abundant VOC in groundwater of this area. Other gasoline-derived contaminants such as benzene, which are less mobile and less recalcitrant than MTBE have never been found. The detection of only MTBE may indicate that none of the wells has been influenced by a near point source. A diffuse input of MTBE with groundwater recharge is more likely.

Achten and Puettmann recently reported concentrations of 7-160 ng/L (median 67 ng/L) in several German rivers (35). Concentrations of MTBE in 12 samples from the Elbe, Saale, and Mulde rivers as well as smaller rivers and two ponds in Leipzig, Germany, were found to be up to 200 ng/L (36). Downstream a MTBE manufacturing plant's outflow into river Lippe, Germany, MTBE concentrations ranged from 200 to 500 ng/L. Higher maximum concentrations than in German rivers were reported from 3 out of 11 river sampling stations in Kanton Zuerich, Switzerland (32). In Helsinki,

Table IV. **Available background concentrations of MTBE in ground- and drinking water in Europe**

Country	Region (if specified)	Year	Number of samples / positives[a]	Concentration range of positives (in µg/L)	Reference
Denmark	n.a.	1997	22/7	0.1-0.6[b]	(29)
Denmark	County of Funen	2000	20/7	0.1->30	(30)
Germany	Urban areas	1999	90/48	n.a.	(31)
Germany	Rural areas	1999	90/8	n.a.	(31)
Switzerland	Kanton Zuerich	1996-1999	400/43	0.06-0.81	(32)
Switzerland	other Kantons	1998-2000	65/6	0.06-0.13	confidential
UK	n.a.	1992-1996	151/13	0.06-2.9	(33)
UK	n.a.	1992-2000	1178/623	0.1-1[c]	(34)

n.a.: no data available
(a): LOD range 0.05 to 0.2 µg/L
(b): one sample had an exceptionally high concentration of 30 µg/L
(c): 10 additional samples had concentrations of 1-5 µg/L, 3 samples above 5 µg/L. At the latter sites, point source influences were reported.

Table V. Available concentrations of MTBE in European surface water bodies

Country	Water body (if specified)	Year	Concentration range (in µg/L)	Reference
Denmark	Lakes (used as drinking water reservoir)	1998	< LOD - 0.59	(29)
Finland	Creeks and rivers Helsinki area	1998/99	0.2 - 0.5	(2)
Finland	Helsinki boat harbor (sea water)	1999	0.4 - 6.1	(2)
Germany	Various rivers	1999	0.007-0.2	(35, 36).
Switzerland	Lake Zuerich (boating activities)	1999	< LOD - 1.4	own work
Switzerland	Rivers Kanton Zuerich	2000	< LOD – 0.45 (2.5[a])	(32)

LOD: Limit of Detection

(a): The high value of 2.5 µg/L was only measured once
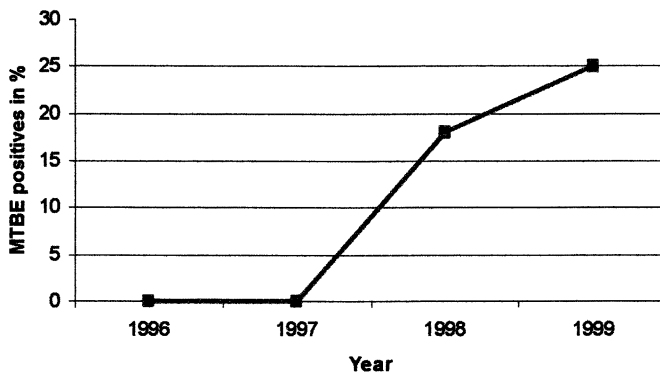
Figure 2.   MTBE detection in groundwater over time in Kanton Zuerich, Switzerland

Finland, average concentrations of 420 to 480 ng/L were measured in two urban creeks subject to diffuse emissions, e.g. from storm run-off (2). In the river Vantaanjoki, a concentration of 190 ng/L was measured at a sampling point downstream from Helsinki.

The available studies show that concentrations of MTBE in running water are not expected to exceed 500 ng/L. Higher concentrations are indicative of a recent spill event.

For Helsinki harbor, MTBE concentrations in sea water of up to 6 µg/l were reported which is comparable to the findings of Reuter et al. (26) in the US. In Lake Zuerich, Switzerland, MTBE concentrations near the surface were up to 1.4 µg/L during a period of intense boating activities on the lake. Other fuel oxygenates were not detectable, benzene concentrations were in the same range. During the boating season, Lake Zuerich is stratified and water exchange between epilimnion and hypolimnion is slow. MTBE is therefore hardly transported to deeper layers of the lake and is rapidly eliminated by partitioning to the atmosphere. Modeling of MTBE behavior shows that MTBE concentration in the epilimnion is already below 10 ng/L before mixing of lake water occurs in winter.

In conclusion, drinking water supplies from lakes are hardly influenced by MTBE emitted during regular boating activities if the lake is stratified during the boating season and drinking water is collected from below the thermocline.

Point source releases

Some authorities and industry representatives in Europe claim that the strict regulation of USTs in Europe prevents the problems seen with MTBE in

the US. This view is questioned by an increasing number of reports on point-source releases from current or former leakages at gasoline stations and storage facilities that led to contamination of groundwater with MTBE (see examples of site-specific data in Table VI). However, statistics on UST leakage related groundwater contamination with MTBE in Europe are not available. In addition to leaks, transport accidents also quite often lead to spills of gasoline that may reach groundwater but the contribution of accidental spills to the overall number and significance of point sources cannot be estimated at the present time.

In Denmark, MTBE has been monitored in groundwater for several years in areas that could be influenced by releases from gasoline storage tanks. Local authorities reported contamination of shallow aquifers with MTBE in the vicinity of four out of five gasoline stations in 1997 (4) and 62 out of 72 stations in a recent investigation in the County of Funen (30). A measuring campaign by Danish oil companies found MTBE in groundwater at three out of four suspected gasoline release sites (4).

MTBE was also found in groundwater samples from three out of four investigated Dutch gasoline stations. The highest MTBE concentration measured was 120 µg/L (38).

At a site in Zuerich, Switzerland, the contamination of a pleistocene gravel aquifer with MTBE due to a spill of gasoline from a derailed tank-wagon train has been studied over a longer period of time (39). With respect to future site use, diffusion of residual gasoline vapours into residential buildings was considered the critical exposure pathway at this site. Remediation by soil vapor extraction was performed for three years after the accident. MTBE became a critical parameter for groundwater risk assessment due to its high mobility and resistance to biodegradation in the subsurface. Mass balance calculations suggested that even after clean-up (excavation and soil venting) significant amounts of MTBE remained in the soil or entered the groundwater. Since observed concentrations of MTBE in groundwater downgradient of the spill site were lower than had been expected from model calculations, biological degradation of MTBE has been suggested as an explanation. Results from two monitoring wells in the downgradient direction of the spill location over time show peak concentrations of 123 and 2.72 mg/L at a distance of 40 and 250 m from the source, respectively. The data indicate that the mass center of the MTBE plume has been transported downgradient with the groundwater flow.

At another site in Zuerich, Switzerland, a tank lorry spilled several thousand liters of gasoline in an industrial area in 1998 (40). Average contents of MTBE and benzene in the spilled gasoline were 9.6 and 4 %, resulting in calculated aqueous saturation concentrations of 5600 and 93 mg/L, respectively. Most of the fuel was recovered but about 1500 L remained in the subsurface and contaminated the groundwater, which was extracted at the spill site and about 20 m downgradient. Maximum measured concentrations of MTBE at the downgradient extraction well were > 1000 µg/L whereas benzene

Table VI. Representative concentrations of MTBE in groundwater influenced by point sources

Country	Incident(s)	Year	Maximum observed concentration (in µg/L)	Reference
Denmark	Leaks at gasoline stations	1997/98	550000	(29)
Denmark	Leaks at gasoline stations	2000	53000	(30)
Finland	Leaks at gasoline stations	1996-1998	330000	(2)
France	Spill	1996	2000	(37)
Germany	Leaks at storage facilities/refineries	1998/99	185000	(1)
Germany	Vicinity of gasoline stations	1999	1000	(31)
Germany	Leaks at gasoline stations	2000	87000	(36)
Netherlands	Leaks (?) at gasoline stations	1999	120	(38)
Switzerland	Spill	1994	123000	(39)
Switzerland	Spill	1998	>1000	(40)
Switzerland	Spill	2000	6000	own work
Switzerland	Spill	2000	165000	own work
UK	Leaks at gasoline stations	1996-2000	830000[a]	(34)

(a): free phase petrol in sample supected

concentrations never exceeded 1-2 µg/L. This field site represents typical behavior for a gasoline spill in an aerobic, fairly permeable aquifer. While benzene is degraded fast enough to prevent spreading far from the source zone, the MTBE plume spreads out and its mass center moves beyond the monitoring well.

In Germany, UBA has recognized significant MTBE contamination from two larger storage facilities and one gasoline station. One of the storage facilities is located at a former military base of the Soviet Army that was abandoned in 1992. MTBE was found in concentrations up to 2 mg/L. The other site is the large petrochemical plant in Leuna, Saxony-Anhalt. In the highly polluted groundwater of this area, MTBE was measured in a maximum concentration of 185 mg/L, and significant amounts of MTBE have been transported downgradient and infiltrated into the nearby Saale river. A concentration of 200 µg/L MTBE was measured in groundwater close to a gasoline station in Bavaria (1). MTBE was also found in groundwater samples from four sites of known point source releases of gasoline (three service stations and one facility for gasoline storage and handling). At a detection limit of 10 ng/L, MTBE was found in all of the 23 samples analysed, with maximum concentrations at the four sites ranging between approximately 1.9 and 87 mg/L (36).

In the UK, a joint report of the UK Environment Agency and the Institute of Petroleum (34) showed MTBE contamination at 179 out of 292 gasoline stations and distribution terminals for which detailed information on potential MTBE occurrence was available. However, these numbers are probably not representative of all stations since many of them were selected using previous knowledge on site and spill history.

Although all the data presented here are not necessarily representative, they show that near gasoline stations and storage areas the risk of contamination with MTBE is significant in Europe.

Conclusions and outlook

The lack of representative monitoring data makes it difficult at the moment to evaluate the environmental contamination and risk from MTBE use in Europe, particularly in southern and eastern European countries. The need for a European UST performance study and a European register of fuel transport accidents to provide sufficient data for a conclusive risk assessment is evident. MTBE is to be included in routine monitoring programs of volatile organic compounds and at accidental gasoline spill sites MTBE *and* its major degradation products are to be incorporated in surveillance programs.

In addition to the necessity of monitoring data, main research gaps include
(a) transport pathways of fuel oxygenates in the environment, in particular immission pathways to groundwater,
(b) long-term behavior of fuel oxygenates in the subsurface, with emphasis on monitored natural attenuation and
(c) the use of MTBE as an indicator/tracer for contaminations from gasoline storage and traffic in general

The European risk assessments (EU, CEFIC) concentrate on the compound MTBE. In future studies, it is crucial to include MTBE degradation products such as TBA as well as possible MTBE substitutes (ethanol, ETBE, TAME).

Acknowledgements

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Chapter 6

Health Risk Issues for Methyl *tert*-Butyl Ether

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A substantial database exists on the inhalation toxicity of MTBE, but exposure information and health effects data for non-inhalation routes of exposure are limited. In addition, several issues complicate the interpretation of the available data in assessing the health risks of MTBE. These issues are discussed in terms of non-cancer and cancer health risks. Some current and further activities in support of MTBE health risk assessment are described.

To assess the potential risks of methyl tertiary butyl ether (MTBE) quantitatively, information on the potential for population exposures as well as both qualitative and quantitative information on the health effects of MTBE is needed. Although the focus of MTBE health risk assessment efforts was initially on the effects of inhalation exposures, evidence of groundwater contamination by MTBE has also led to concerns about contamination of drinking water and the potential for human exposure and consequent health effects. In some respects, MTBE health effects have been well characterized, but in other respects significant uncertainties have contributed to the difficulty in resolving debates about the potential human health hazards and risks related to MTBE.

Non-Cancer Health Risks

Several inhalation studies on the toxic effects of MTBE were conducted under provisions of an enforceable consent agreement between EPA and oxygenate manufacturers in the late 1980s and early 1990s (*1*). These studies yielded a substantial amount of information that was evaluated by EPA in deriving an inhalation reference concentration (RfC) for MTBE. The RfC is defined as an estimate (with uncertainty spanning about an order of magnitude) of a continuous inhalation exposure level for the human population (including sensitive subpopulations) that is likely to be without appreciable risk of deleterious non-cancer effects during a lifetime. Reference concentrations have generally been derived from health effects studies by (1) identifying a no-observed-adverse-effect level (NOAEL), lowest-observed-adverse-effect level (LOAEL), or an alternative benchmark value obtained through mathematical analysis of the data; (2) adjusting this concentration to reflect continuous human exposure; and (3) dividing the adjusted concentration by uncertainty factors (UFs) as appropriate for extrapolations across species, to sensitive subpopulations, from subchronic to chronic exposures, or for other limitations in the available data.

The original RfC for MTBE was initially based primarily on effects observed in rats exposed by inhalation for 13 weeks to concentrations of 2,880, 14,400, or 28,800 mg/m³ MTBE (*2*, subsequently published in *3*). Various "moderately adverse" effects in different organ systems (brain, adrenal, female kidney, and liver), along with decreased body weight, were cited as the basis for an RfC of 0.5 mg/m³ MTBE (*4*). After the results of 2-year bioassays became available, EPA revised the RfC in 1993, based on findings of increased liver and kidney weights and increased severity of spontaneous renal lesions in female rats, as well as increased prostration in females and swollen periocular tissue in male and female rats (*5*, subsequently published in *6*). The concentrations in the chronic study were nominally 1,440, 10,800, and 28,800 mg/m³ MTBE . Although the NOAEL was lower in the chronic study (1,440 mg/m³) than in the subchronic study (2,880 mg/m³), the total UF used in deriving the revised RfC was 10-fold lower because no UF was needed for extrapolating from subchronic to chronic exposure. Thus, after adjusting the NOAEL for continuous duration exposures and dividing by a total UF of 100, the RfC for MTBE is 3 mg/m³ (*7*).

Although adequate exposure data on population exposures to MTBE were not available, the U.S. Environmental Protection Agency (*8*, *9*) considered various "worst case" scenarios and estimated potential long-term average exposure levels to MTBE in relation to both winter oxyfuel (containing 15%-vol MTBE) and year-round reformulated gasoline (containing 11%-vol MTBE). These worst-case

average exposures were less than 0.2 mg/m³, or about an order of magnitude below the RfC of 3 mg/m³. Thus, based on the available information, EPA (9) concluded that "long-term exposures to MTBE vapors are not expected to cause adverse non-cancer health effects, but effects of...mixtures of gasoline and MTBE...are unknown." This conclusion was essentially affirmed by subsequent reviews and assessments by other organizations (10-13).

When oxygenated gasoline was first introduced in late 1992, complaints of headache, nausea, eye and nose irritation, and other health symptoms were registered in Fairbanks, Alaska, and a few other locales. These health complaints were associated with acute exposures to MTBE-oxygenated fuel. Although several studies were initiated in response to these complaints, a basis for the acute symptoms attributed to MTBE has not been established. These studies included experimental investigations with laboratory animals (e.g., 14) as well as human volunteers (e.g., 15-17). In addition, epidemiological studies were conducted in communities where MTBE-oxygenated fuels were used (e.g., 18, 19). However, none of these studies investigated the reactions of self-reported sensitive (SRS) individuals under controlled conditions. The only experimental study of such individuals to date is that of Fiedler et al. (20). Twelve SRS subjects were compared to 19 control subjects under four exposure conditions: clean air, gasoline alone, gasoline with 11%-vol MTBE, and gasoline with 15%-vol MTBE. Compared to control subjects, the SRS subjects reported significantly more symptoms of all types (including some not previously associated with complaints about MTBE) under all conditions, including clean air. Apart from these subjective reports, the SRS and control subjects did not differ on objective measures (neurobehavioral or physiological responses) or in their ratings of the odors of the exposure conditions. The SRS subjects did, however, report significantly more symptoms (but no other objective response measure) when exposed to 15%-vol MTBE-gasoline than to clean air or, for that matter, 11%-vol MTBE-gasoline. Thus, the SRS subjects appear to have been more "sensitive" to (15%-vol) MTBE-gasoline, and this differential symptom response does not appear to have been mediated by an ability to discriminate the different exposure conditions by odor. On the other hand, the lack of difference in symptom reports between 11%-vol MTBE-gasoline and gasoline alone (or even clean air) suggests that an MTBE-oxygenated reformulated gasoline, which is the predominant use of MTBE in the United States, would probably not pose a problem for these SRS individuals, assuming their actual exposures are comparable to the test conditions.

Cancer Risk

The potential for MTBE to cause cancer also has been a matter of consider-able discussion and debate. Three chronic studies have been conducted in laboratory rodents exposed to MTBE by either the inhalation route or oral route. Two inhalation studies (6) were conducted, one with rats and the other with mice

exposed to 0, 1440, 10,800 and 28,800 mg/m³ MTBE 5 days per week for 24 months (rats) or 18 months (mice). The oral bioassay (21) was conducted with rats given MTBE in olive oil by gavage at doses of 0, 250, and 1000 mg/kg body weight once daily for 4 days per week for 24 months. Various types of tumors were observed in these studies: liver tumors in female mice exposed by inhalation, kidney tumors in male rats exposed by inhalation, testicular tumors in male rats exposed by either inhalation or ingestion, and lymphomas and leukemia in female rats exposed by ingestion. Each of these findings has had some degree of uncertainty surrounding it.

The female mouse liver tumors have been viewed by some experts as an indirect consequence of a disinhibitory effect of MTBE, in which MTBE disrupts the normal suppressive effect of estrogen on liver tumor induction (22). This interpretation implies that MTBE is a tumor promoter rather than a tumor initiator and that tumor induction is likely to occur at some threshold level, which would have important implications for how the cancer risk is estimated quantitatively. Rather than assuming a linear concentration-response relationship that extrapolates to zero, the potency estimate would be lower if effects were only observable at much higher concentrations. Although subsequent work (23, 24) has not fully supported the tumor-promoter hypothesis, neither has it ruled out a threshold-acting mechanism.

In the matter of male rat kidney tumors, considerable research has gone into elucidating the mechanism underlying such tumors and understanding their implications for human cancer risk (25). A protein, alpha-2u-globulin (α-2u), which is found only in male rats, has been shown to cause nephropathy by accumulating in the lysosomes of the proximal tubule cells and inducing cell proliferation and, ultimately, tumors. Several chemicals, including MTBE, can bind to α-2u and thereby reduce the normal breakdown of this protein, but MTBE does so relatively weakly. Borghoff and her colleagues (26-29) have amassed several lines of evidence that α-2u mediates the formation of male rat kidney tumors from MTBE, but the lack of a clear quantitative relationship between α-2u accumulation and ultimate tumor incidence is the primary impediment to concluding that male rat kidney tumors associated with MTBE are solely a function of an α-2u mechanism and therefore not relevant to human cancer risk.

The only commonality among the tumor sites in the three chronic studies is the testicular Leydig cell tumors in rats exposed by either inhalation or ingestion. This concordance of findings usually enhances confidence in the evidence of carcinogenicity. However, alternative explanations for their occurrence have been offered (30). One argument is that, in the inhalation study, an abnormally low incidence of testicular tumors in the control rats (compared to historical controls) accounted for the seemingly significant increase in the exposed rats. Also, in the ingestion study, the fact that the rats were allowed to live beyond the conventional termination date could underlie the occurrence of such tumors, which are known to be more common in older rats and especially prevalent in the strain of rats used in this study. Attempts to investigate a possible hormonal basis for MTBE-

induced testicular tumors have not yet resolved how or whether such a mechanism applies (31).

The lymphomas and leukemias observed in the female rats exposed by ingestion have been a particular focus of critical review (13). Among other things, questions have been raised about the pathological basis for identifying these tumors as well as for combining the tumors for statistical analysis. Belpoggi et al. (32) responded to these questions by providing further information on the nature of these pathological effects, which were all reported to be of lymphatic origin. This suggests that it was appropriate to combine the lymphomas and leukemias for statistical purposes. However, other questions (e.g., decreased survival rates suggestive of exceeding the maximum tolerated dose) were not addressed by Belpoggi et al. (32).

The above findings, along with other information, including the carcinogenicity of two metabolites of MTBE (formaldehyde and tertiary butanol), have been considered by various expert groups in judging the weight of evidence for the carcinogenicity of MTBE. Different groups have come to different conclusions about this evidence. For example, the U.S. Environmental Protection Agency (9, 33), the Interagency Oxygenated Fuels Assessment Committee (10, 11), and the California Environmental Protection Agency (34) have judged MTBE to be a potential cancer hazard to humans. However, other expert bodies, including advisory committees for the World Health Organization (35), the International Agency for Research on Cancer (36), California Proposition 65 (34), and the U.S. Department of Health and Human Services (37), have concluded that the available evidence is insufficient to determine that MTBE poses a carcinogenic hazard to humans.

Current Status and Next Steps

Because the odor and taste detection thresholds for MTBE are relatively low compared to many other common chemicals, organoleptic considerations have been the predominant basis for actions that have been taken thus far at the local, state, and federal levels. Average odor detection thresholds for MTBE in water have been reported to range from 15 μg/L to 180 μg/L (15, 38-42), with most of the average values in the lower half of that range and some individuals' thresholds below 5 μg/L (41). By comparison, the odor threshold for benzene, for example, is about 10-fold higher (39).

The U.S. Environmental Protection Agency (33) issued an advisory for MTBE in drinking water, based on taste and odor characteristics. The advisory suggested that consumer acceptability of water could be maintained if MTBE concentrations were at or below 20– 40 μg/L. The Agency is currently developing a secondary maximum contaminant level (MCL) for MTBE based on odor or taste. A secondary MCL is not an enforceable regulatory standard at the federal level, but some states adopt EPA secondary MCLs as enforceable standards.

The EPA drinking water advisory for MTBE also noted that levels of 20 to 40 µg/L would afford a margin of exposure (safety) of at least 20,000- to 40,000-fold below the levels at which laboratory animals showed adverse health effects. However, the advisory also noted the limitations in the existing database (as discussed above) on which to base quantitative health risk estimates for MTBE in drinking water. One strategy for generating quantitative health risk reference levels applicable to drinking water exposure would be to use the available inhalation health effects data, along with physiologically based pharmacokinetic (PBPK) modeling, to extrapolate from effects via the inhalation route of exposure to the ingestion route (*43*). The relative abundance of PBPK modeling for MTBE (*26, 44, 45*) is expected to aid this cross-route extrapolation, which EPA is currently considering as part of an effort to update the evaluation of MTBE health issues for the Agency's Integrated Risk Information System (IRIS).

From an exposure standpoint, the relatively low detection thresholds for MTBE do not necessarily imply that ingestion of drinking water contaminated with MTBE would be averted solely because of its odor and taste characteristics. Statistically representative samples of populations have not been evaluated for sensory threshold responses to MTBE, but it is well known that sensory acuities are normally distributed, with anosmic individuals at one tail of the distribution (*46*). Although attempts have been made to model drinking water exposure to MTBE and characterize health risks (*47-51*), better empirical data on population exposures to MTBE are needed to support risk assessment efforts (*43*). In addition, human exposure needs to be evaluated from a multi-source, multi-media perspective, integrating across inhalation, dermal, and oral routes.

It is also important to consider the health and exposure issues associated with MTBE in the context of the total life cycle of the product, beginning with feedstocks and production, and continuing through distribution, use, and disposal (*51*). This approach looks beyond the immediate question of the health risks of MTBE per se and considers the potential impacts of by-products and other indirect ramifications. In this manner, the various trade-offs of MTBE, such as those between air quality and water quality impacts, can be brought into sharper focus. Moreover, a complete assessment of this type should be comparative, because the question is not simply whether MTBE is good or bad but whether the trade-offs it presents are better or worse than the trade-offs of other fuel options.

Disclaimer

The views expressed in this paper are those of the author and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.

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tert-Butyl Alcohol: Chemical Properties, Production and Use, Fate and Transport, Toxicology, and Detection in Groundwater and Regulatory Standards

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tertiary-Butyl Alcohol (TBA), a fuel oxygenate and breakdown by-product of Methyl tertiary Butyl Ether (MtBE), is a significant potential groundwater contaminant because of its mobility, recalcitrant nature, and potential toxicity. Exposure to TBA can lead to irritation of mucous membranes, nausea, defatting of the skin, and intoxication. Metabolism of TBA leads to the formation of 2-methyl-1,2-propanediol which is oxidized to 1-hydroxybutyrate or to formaldehyde and acetone. Although TBA is negative in *Salmonella typhimurium* and mouse lymphoma cell mutation tests, and does not induce sister chromatic exchanges or chromosomal aberrations in cultured Chinese hamster ovary cells, it is believed to be a potential carcinogen. TBA is not a substrate for alcohol dehydrogenase and appears to be more slowly metabolized than MtBE. There is currently no Federal drinking water standard for TBA although two states have drinking water action levels for TBA ranging from 100 ug/L to 12 ug/L.

Chemical Properties

Tertiary-Butyl Alcohol (CAS # 75-65-0), also known as TBA, Tert-Butyl Alcohol, T-Butanol, T-Butyl Hydroxide, 1,1-Dimethyl Ethanol, Trimethyl

Methanol, 2-Methyl-2-Propanol, and Trimethylcarbinol, is an alkylated alcohol with the structural formula $(CH_3)_3COH$ and a molecular weight of 74.1 g/mol. It is manufactured by the catalytic hydration of isobutylene or by the reduction of tert-butyl hydroperoxide.

The chemical and physical properties of TBA are summarized in Table I. There are a number of sources of information and, based on the literature reviewed, the values cited in Table I are representative. Some minor variations from the values presented in Table I may be expected.

Table I. Chemical And Physical Properties Of TBA

Property	Value	Unit	Reference
Structural formula	$(CH_3)_3COH$		1
Molecular weight	74.1	g/mol	Calculated
Melting point,	25.7	°C	1
Boiling point	82.41	°C	1
Specific gravity (20/4 °C)	0.786	unitless	1
Density (20 °C)	0.79	g/ml	1
Aqueous solubility (20 °C)	Soluble	mg/L	
Vapor pressure (25 °C)	42	mm Hg	2
Solubility in gasoline	miscible	--	3
log K_{ow}	0.35	unitless	2
log K_{oc}	1.57	unitless	2
Henry's law constant (25 °C)	0.000503		4
Henry's law constant (5 °C)	0.000113		4
Flash point	11.1	°C	1
Conversion Factor (in air)	1 ppm = 3.08 mg/m^3		Calculated
Odor	Camphor-like		1
Odor Threshold in Air	47-600	ppmv	3

TBA is a volatile (42 mm Hg at 25 °C), flammable, and colorless liquid at room temperature. TBA is miscible in gasoline, ethers, and other alcohols. It has a specific gravity of approximately 0.79 (at 25 °C) and, as a result, free-phase TBA will float on water. TBA is soluble in water. The unitless Henry's Law constant for TBA at 5 °C and 25 °C is 0.000113 and 0.000503, respectively (4). Thus, dissolved TBA does not easily partition from water to air.

The low organic-water partitioning coefficient (K_{ow}) of 0.35 given for TBA (2) indicates that TBA is not likely to accumulate to a significant degree in human or animal fat tissue. The organic-carbon partitioning coefficient (K_{oc}) of

a substance is the partition coefficient defined as the ratio of adsorbed chemical per unit weight of organic carbon in a saturated medium to the aqueous solute concentration (5). The low K_{oc} of 1.57 given for TBA (2) means that TBA is unlikely to be attenuated by aquifer materials or to adsorb well to granulated activated carbon (GAC).

Production And Use

TBA is used as a denaturant for ethanol, in the manufacture of floatation agents, flavors, and perfumes (especially in the preparation of artifical musks); as a solvent, in paint removers; and, as an octane booster in gasoline (2). TBA is also used as a solvent for pharmaceuticals, as a dehydrating agent, and in the manufacture of methyl methacrylate (6). It is a raw material in the production of isobutylene, which may be used to produce methyl tertiary butyl ether, a common gasoline additive, or to produce butyl elastomers used in the production of automobile tires. TBA is used in the purification of polyoelfins, for the separation of solids from coal liquids and as a blowing agent for the manufacture of imide group-containing foams from copolymers of methacreylonitrile and methacrylic acid (7). TBA may be formed in the environment through oxidation of MtBE in the atmosphere followed by hydrolysis or through microbial oxidation of MtBE in impacted aquifer materials.

Use As A Fuel Oxygenate

After tetraethyl lead was phased out in the 1980's by the United States Environmental Protection Agency (USEPA) as an anti-knock agent in gasoline, refiners looked to oxygenates to replace the octane loss in gasoline. Small quantities of oxygenates added to gasoline replace significant amounts of octane.

MtBE is currently the most commonly used fuel oxygenate because of its low cost, ease of production and transfer, and its blending characteristics (8). After several high profile MtBE releases came to light (Cities of Santa Monica, Marysville, Glenville, Santa Clara), refiners of RFG have searched for acceptable substitutes for MtBE. Table II provides a list of the key oxygenates proposed or used by gasoline refiners along with the key physical properties for refiners.

TBA has an octane rating of about 100, lower by approximately 10 numbers than MtBE, but higher than most gasoline blending components. Alcohols like TBA or ethanol, increase the volatility of gasoline so that mixtures of gasoline and TBA alone will not comply with reformulated gasoline specifications for gasoline volatility, unless steps are taken to adjust the volatility of the blend (9).

Table II. Key Physical Properties of Oxygenates[10]

Oxygenate	Blending Octane (R+M)/2	Blending RVP (psi)	Boiling Point (F)	Oxygen Content (%)	Water Solubility (%)
Ethers					
MtBE	110	8.0	131	18.2	4.3
TAME	105	2.5	187	15.7	2.0
ETBE	112	4.0	161	15.7	1.2
IPTBE	113	2.5	188	13.8	Na
TAEE	100	1.0	214	13.8	Na
DIPE	105	5.0	155	15.7	2.0
Alcohols					
Ethanol		18.0	173	34.8	Infinite
TBA	100	9.0	181	21.6	Infinite
Iso-Propanol	106	14.0	180	26.7	Infinite
Iso-Butanol	102	5.0	226	21.6	10.0
TAA	97	6.0	216	18.2	11.5

NOTE:

na=not available

TBA=Tertiary butyl alcohol

DIPE= Di-isopropyl ether

IPTBE=Iso-Propyl Tertiary Butyl Ether

TAEE=Tertiary Amyl Ethyl Ether

TAA = Tertiary Amyl Alcohol

Gasoline grade TBA (GTBA) was first used by Atlantic-Richfield Company (ARCO) as an octane enhancer in 1969 (3). In 1979, USEPA approved the use of GTBA in ARCO gasoline in concentrations up to 7.0%. Sun Oil Company also received a waiver from USEPA to blend equal volumes of ethanol and GTBA (up to 2.75%) in unleaded gasoline. ARCO later received another waiver from USEPA to blend methanol and GTBA in gasoline in 1:1 ratios up to 9.5% by volume. Other waivers were granted by USEPA for blends of gasoline and GTBA up to 3.5 mass percent oxygen content (16% by volume TBA) and for various blends of methanol and GTBA or other higher-molecular-weight alcohols (co-solvents) (3).

Fate And Transport

After a release of TBA-blended gasoline, such as from a leaking underground storage tank (LUST) or a pipeline, TBA will partition from the free-phase by volatilization into the gas phase due to its high vapor pressure and by dissolution into soil water due to its aqueous solubility. For TBA to volatilize into the atmosphere, the release must be at or near the surface of an unsaturated soil. The mass of TBA that partitions to the atmosphere will vary as a function of infiltration rate, soil moisture, and surface temperature. Minimum volatilization will occur with a fast infiltration rate, high soil moisture, and low surface temperature. However, since TBA readily transfers to percolating soil water, most of the TBA mass would be expected to be present in the groundwater, within a few years after a TBA-blended gasoline release.

Fate And Transport In Air

Three processes may control the fate of TBA in the atmosphere. The first is atmospheric washout of TBA in rainwater. The second is photooxidation of TBA. The third is reaction of TBA with NO.

As noted by Zogorski et al. (11), fuel oxygenates like TBA will tend to partition into atmospheric water, including precipitation. Atmospheric washout of TBA in rainwater is likely to be a significant fate process for TBA releases to air. A half-life of 34.5 hours, based on the reaction of TBA with NO, is reported by Dilling (12). The half-life for the reaction of vapor phase TBA with photochemically generated hydroxyl radicals was estimated by USEPA to be 1.09 months (2).

Fate And Transport In Soil

TBA can enter soil water or groundwater either from direct dissolution of TBA-blended gasoline, or through dissolution from TBA in the gas phase. Since TBA has a high solubility, it readily partitions into the dissolved phase. Furthermore, due to its moderately low Henry's Law constant, TBA resists volatilization from groundwater into the gas phase. Since the K_{oc} for TBA is low, it will not significantly sorb to soil organic matter. Further details regarding the fate of TBA in groundwater is discussed below.

Fate And Transport In Groundwater

TBA has the potential to be an important groundwater contaminant because of its mobility, recalcitrant nature, and potential toxicity. Once a spill of

reformulated gasoline containing TBA occurs, TBA and other gasoline compounds dissolve into the groundwater and are subject to movement through the natural hydraulic gradient. Plume movement will occur preferentially through materials of high hydraulic conductivity such as sand and gravel aquifers. Zones of low hydraulic conductivity, such as clays and silts, will limit horizontal and vertical contaminant movement if these sediments are unfractured. The movement of the contaminant mass is limited by abiotic and biotic processes that attenuate and/or reduce contaminant mass, such as dilution, dispersion, adsorption, volatilization, and bio-degradation. Adsorption to organic carbon is the most common attenuation mechanism for dissolved hydrophyllic compounds. Bio-degradation can also lead to contaminant mass loss and, in many instances, a reduction in toxicity for some organic compounds.

Solubility Of TBA

Pure phase aqueous TBA is infinitely soluble in water (Table I). According to Raoult's Law, the solubility of a compound in a mixture is a function of its pure phase solubility times its mole fraction in the mixture (assuming activity coefficients of 1); therefore, the solubility of TBA will be reduced when mixed with gasoline.

Attenuation of TBA Due to Sorption

Since TBA has a low affinity for organic carbon ($K_{oc} \sim 1.57$; Table I), very little retardation occurs as a result of adsorption onto soil organic matter.

Therefore, in a TBA-blended gasoline spill, the leading edge of TBA will be in front of the benzene plume, and this distance will increase with time. Sorption and biodegradation cause the benzene plume to eventually reach steady-state conditions and to cease moving forward. However, since TBA does not sorb noticeably or undergo biodegradation readily (see below), its plume continues to move forward, significantly beyond the edge of the benzene plume. Its movement and size will be limited by dilution, dispersion, volatilization, and possibly biodegradation, but not nearly to the extent of benzene or other aromatics contained in the TBA-blended gasoline.

Bio-degradation of TBA

TBA is reported to persist in active microbial systems, even in microcosms where EtBE is undergoing rapid degradation (13). TBA resistance to biodegradation is consistent with reports by Hickman and others (14,15,16). When biodegradation does occur, anaerobic degradation of TBA is strongly

dependent on the initial concentration and the indigenous microbial activity (14). The difficulty with TBA degradation is the resistance to microbial attack of tertiary or quartenary atoms (16).

Toxicological Properties

This section provides an evaluation of the available information on the toxicological properties of TBA, with a particular focus on its potential to cause adverse health impacts to humans at environmental concentrations. There is little information concerning the toxicity of TBA to human populations; however, there is some information available from animal studies conducted in laboratories. Animal studies are often used as predictors of potential adverse health effects in humans.

Human Studies

Exposure to TBA can occur via inhalation, ingestion, and eye or skin contact. TBA is known to cause eye, skin, and mucous membrane irritation in humans; at high concentrations, it may cause narcosis. Dermal contact may cause slight redness and hyperemia; prolonged skin contact may cause contact dermatitis [17, 18]. Exposure to "excessive" (not further specified) concentrations is reported to have caused eye, nose, and throat irritation, headache, nausea, fatigue, and dizziness in humans [17].

Epidemiological and Clinical Studies

There are no relevant studies of long term exposure or sensitive populations to TBA. When TBA was applied to the skin of human volunteers, no reaction other than slight erythema and hyperaemia was observed (19). Edwards and Edwards (20) described an allergic skin reaction to TBA in a 58-year old patient who used sunscreen containing TBA. A patch test was positive for TBA. There are no other published reports of adverse health effects or poisonings in humans.

Animal Studies: Acute Exposure Studies (Less than 14 Days)

Animals exposed to TBA vapors may manifest the following signs of intoxication: restlessness, irritation of mucous membranes, ataxia, proscration, and narcosis (21). After intraperatoneal (IP) administration of TBA to mice, the lethal dose for fifty percent of the test population (LD$_{50}$) was greater than 1000

mg/kg at 30 minutes and 441 mg/kg at 7 days. Post-mortem examination of the livers showed abnormal dark coloration (22).

Inhalation Exposures:

Whole-body inhalation exposures of rats and mice showed significant decreases in body and organ weights for animals exposed at the highest concentrations (23). Inhalation exposure of rats and mice to TBA resulted in deaths following a single 7,000 ppm exposure and clinical findings of alcohol toxicity (hyper- and hypoactivity, ataxia) at concentrations of 900 ppm and greater in rats and 1,750 ppm and greater in mice. Longer exposures (13-weeks) to concentrations up to 2,100 ppm, lead to increased kidney weights, which correlated microscopically to increased severity of chronic nephropathy. Reproductive parameters in male and female rats and mice were unaffected and the results of all tests for genetic toxicity were negative (23).

Dermal Exposures:

Prolonged contact of TBA with the skin of rabbits caused no irritation [17].

Oral Exposure

Narcosis was observed in animals dosed with high concentrations of TBA. The oral LD_{50} in rats is 3,500 mg/kg [24]. Acutely poisoned animals showed behavioral effects, ataxia, and other narcotic signs before death [24, 25]. TBA is reported to have a stronger narcotic effect on mice than other butyl alcohols [26]. TBA caused a narcotic effect estimated to be 4.8 times greater than that of ethanol when rats were given nontoxic doses of TBA [17].

In Vitro Studies:

TBA has been shown to be a hydroxyl radical scavenger and, therefore, an inhibitor of prostaglandin biosynthesis (27,28).

Other Routes of Exposure:

IP administration of TBA followed by exposure to vapor concentrations of between 50 to 80 μmol TBA/liter of air for 24 hours per day; concentrations

below or above these limits did not produce physical dependence or were initially too toxic (29). Withdrawal signs were noted after removing the mice from the inhalation exposure. The intensity of the withdrawal reaction increased with the duration of inhalation and with the blood-TBA levels maintained during the intoxication period. The withdrawal syndrome was qualitatively similar to that produced by ethanol. McComb and Goldstein (29) concluded that the dose of alcohol necessary to induce physical dependence was inversely proportional to its solubility.

In a study by Bellin and Edmonds (30), symptoms of physical dependence were induced in rats and guinea pigs given TBA IP (0.8 g/kg body weight as a 10% w/v solution) at 8-hour intervals for 4 days. Alteration of body temperature (decreased during intoxication and increased during withdrawal) was more pronounced in the rats than in the guinea pigs.

Neurological Effects:

TBA was shown to deplete the cerebral calcium level in rats given an IP dose of 2g/kg body weight (31).

Developmental Effects:

Pregnant mice fed liquid diets containing TBA up to 1.0 g/liter lead to development delay in post-parturition physiological and psychomotor performance scores of pups. At higher concentrations, there were also significant effects on the dames which altered lactation and/or nesting behavior, which in turn influenced the postnatal development of pups exposed to TBA *in utero* (32).

Hepatic Effects:

Rats administered IP doses of aqueous TBA (250 g/L) showed an increase in carbon tetrachloride-induced hepatotoxicity, as evaluated by serum glutamate-pyruvate transaminase levels. However, there was no depletion in hepatic glutathione or loss in body weight (33). TBA can potentiate the toxicity of carbon tetrachloride in Sprague-Dawley rats (34).

Partially hepatectomized rats given 15% (w/v) aqueous TBA (2.8 g/kg body weight) by gastric intubation showed an inhibition of the synthesis of ornithine

decarboxylase (ODC) and tyrosine aminotransferase (TAT). ODC and TAT are biomarkers of cellular proliferation. In the liver, 4 hours after the partial hepatectomy, the ODC activity was decreased to 22% and the TAT activity to about 52% of the activities in the control group. In the kidney, 4 hours after, partial hepatectomy, the ODC activity was decreased to about 31% of the activity in the control group. In the brain, TBA did not induce any significant changes in the ODC activity compared with that in the control group (35).

Animal Studies: Chronic Exposures (Greater Than 90 days)

Oral Exposures:

Rats exposed to TBA in water as their only available fluid at concentrations of 3.5 ml/liter, were found to have severe toxic reactions, including anorexia, self mutilation, and death. When animals consumed at least 3 grams of TBA/kg body weight per day for 90 days (TBA concentrations of 3% or greater), withdrawal symptoms were observed (36). In female Sprague Dawley rats, TBA administered by gastric intubation, every 8 hours, for up to 6 days, was shown to produce symptoms of physical dependence (37).

Aquatic Toxicity

Water quality criteria to protect aquatic life have not been established by USEPA. A review of USEPA's AQUIRE database on toxicity data of fuel oxygenates by Zogorkski et al. (11) showed that TBA and MtBE appear to have a lower toxicity than other fuel oxygenates, based on the LC_{50}. The LC_{50} for TBA ranges from 2,450 to 6,410 mg/L, compared to 672 mg/L for MtBE (as reported in by Zogorski et al (11)).

Carcinogenicity

Renal tubular cell adenomas and carcinomas were observed in animals administered TBA in drinking water for two years (23). It has been postulated that the tumors may be secondary to cell toxicity caused by TBA (23). The California Environmental Protection Agency's Office of Environmental Health and Hazard Assessment's (OEHHA) reviewed the National Toxicology Program (NTP) drinking water study and has determined that TBA is potentially carcinogenic. OEHHA noted that NTP concluded that "there was 'some' evidence of carcinogenic activity of TBA... based on increased incidences of renal tubule adenoma or carcioma (combined). (38)." The International Agency for Cancer Research and USEPA have not determined whether TBA is a potential carcinogen.

Genotoxicity

At concentrations of 1%, TBA was classified among chemicals that had no apparent mutagenic effect on the formation of anti-biotic resistant mutants in *Micrococcus aureus* populations (39). TBA was not mutagenic in *Neurospora crassa* (40).

Whole body exposure of rats and mice to TBA (23) produced negative results for induction of genetic damage in vitro and in vivo. In vitro, TBA was negative in *Salmonella typhimurium* and mouse lymphoma cell mutation tests, and it did not induce sister chromatic exchanges or chromosomal aberrations in cultured Chinese hamster ovary cells (23). These in vitro studies were conducted with and without metabolic activation (S9). In vivo, no increase in the frequency of micronucleated erythrocytes was observed in peripheral blood samples from mice administered TBA in drinking water for 13 weeks. Also, induction of micronucleated erythrocytes was noted in bone marrow cells of rats administered TBA by intraperitoneal injection (23).

Toxicokinetics

TBA is not a substrate for alcohol dehydrogenase (7) and is slowly metabolized by mammals. Up to 24% of the dose is eliminated in the urine as glucuronide and up to 10% of the dose can be excreted in the breath and urine as acetone or carbon dioxide. The primary acute effects observed in animals are signs of alcoholic intoxication.

TBA appears to be metabolized more slowly than MtBE, with glucuronidation being an important pathway for its elimination. Metabolism of TBA leads to 2-methyl-1,2-propanediol, which is further oxidized to either 1-hydroxybutyrate or to formaldehyde and acetone. Following exposure to MtBE, levels of TBA in blood are similar to or higher than the corresponding levels of MtBE . Although both MtBE and TBA appear to be reliable indicators of MtBE dose, further studies are needed to establish the time course of their blood or urine concentration as a function of the exposure concentration before either one can be used as a marker of exposure in human studies (41).

Drinking Water Standards For TBA

Currently there is no Federal drinking water standard for TBA. Two states, California and New Jersey have action levels for TBA. The Calfornia Department of Health Services (CDHS) established a Drinking Water Action

Level of 12 µg/L for TBA in 1999. Drinking Water Action Levels are health-based advisory levels established by CDHS for chemicals for which primary maximum contaminant levels have not been adopted.

New Jersey issued an Interim Specific Groundwater Criterion (ISGC) of 100 µg/L for TBA in September 1997. New Jersey had lowered the groundwater cleanup criteria from 500 µg/L to 100 µg/L, based on the 1995 National Toxicology Program TBA drinking water study of rats and mice.

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Chapter 8

Ethyl *tert*-Butyl Ether and Methyl *tert*-Butyl Ether: Status, Review, and Alternative Use

Exploring the Environmental Issues of Mobile, Recalcitrant Compounds in Gasoline

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Petroleum products from leaking underground storage tanks have raised concerns regarding the quality of groundwater resources. The concerns about the environmental behavior and fate of MTBE as an oxygenated additive prompted this investigation to explore the technical characteristics of MTBE in comparison to ETBE. Evaluation of the existing literature suggests that ETBE has more favorable characteristics than MTBE. Findings in this research suggest that ETBE is a technically sound oxygenated octane enhancer, which can help refiners meet specifications for cleaner burning gasoline.

Petroleum products from leaking underground storage tanks have raised concerns regarding the quality of groundwater resources. Although many of the components of gasoline may be retained in soils by adsorption and eventually degrade, the more water-soluble components such as methyl tert-butyl ether (MTBE) spread through groundwater. Of the 60 volatile organic compounds analyzed in samples of shallow ambient groundwater that were collected from eight urban areas during 1993-94 as part of the U.S. Geological Survey's National Water-Quality Assessment program, MTBE was the second most

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frequently detected compound (1). This is more alarming considering the fact that MTBE is a relatively new additive in the fuel market.

Evaluation of the existing literature suggests that ETBE has more favorable characteristics than MTBE. Blending studies show ETBE to have an advantage over MTBE because of lower vapor pressure, and higher octane boost. ETBE has lower oxygen content than MTBE. To achieve a certain level of oxygen in gasoline more ETBE is added, thereby reducing the concentration of other compounds targeted for reduction in the gasoline stream such as aromatic compounds. ETBE also allows for the use of more butane in gasoline without vapor pressure penalty.

Experimental studies for the remediation of MTBE and ETBE contaminated water confirm the preliminary research findings. Both air stripping and carbon adsorption were more favorable for the removal of ETBE from the contaminated water compared to MTBE. ETBE has a lower solubility in water than MTBE and due to its stronger partitioning from water to air, ETBE is removed faster than MTBE from the contaminated water.

Physical Characteristics of MTBE and ETBE in Water

The effectiveness of remediation methods for the removal of certain constituents from water is directly linked to the physical characteristics of the constituents of interest. Water solubility and volatilization are two of the most important properties affecting the partitioning of organic compounds between water and air.

Water Solubility

Both MTBE and ETBE tolerate very small amounts of water and strongly favor the hydrocarbon phase. MTBE and ETBE tolerate very small amounts of water, 1.4 and 0.6 wt % at 20 C, respectively (2,3). However, unlike alcohols that are hygroscopic and tend to separate into the aqueous phase, ethers strongly favor the hydrocarbon phase in the presence of water. Gasoline-ether blends shed water similar to a typical gasoline and very little ether is extracted from the gasoline (4). This is also due to a relatively low solubility of ethers in water. The solubility of MTBE and ETBE in water are reported as 4.3 and 2.0 wt % at 20 C, respectively (2,3). Lower solubility of ETBE in water and water in ETBE compared to MTBE suggests a lower water tolerance in an ETBE-gasoline blend and also lower extraction of ETBE in the presence of water.

Effect of MTBE on Enhancing the Solubility of Hydrocarbons in Water

The effect of oxygenate additives such as methanol, MTBE, and ethanol on the aqueous solubility of BTEX compounds has been evaluated by Mihelcic (5) and Poulsen and co-workers (6). Results for MTBE showed an increase in the solubility of BTEX compounds in water as the MTBE concentration in water was increased. However, at 0.1 % concentration of MTBE this enhancement in the solubility of the BTEX compounds was insignificant. Since this concentration of MTBE in water is equal to about 100 PPM, it is unlikely that MTBE significantly enhances BTEX solubility in the contaminated groundwater. Data for the enhancement effects of ETBE on hydrocarbon solubility is not available, but ETBE is expected to have a similar effect.

Volatilization of Ethers from Water

The rate of vaporization of organic solutes determines their fate in contaminated surface water (e.g. streams, lakes, reservoirs, and ponds). The manner in which organic compounds volatilize from water has been discussed in the literature (7). Established modeling procedures exist for estimating the vaporization rate of organic compounds. Mass transfer coefficient quantifying this process can be obtained from the two-film model of Lewis and Whitman (8) and the equations developed by Rathbun and Tai (9) for predicting the liquid-film and gas-film reference-substance parameters.

Pankow and co-workers (10) used the two-film theory of diffusion and the reference-substance concept (7) to estimate the volatilization rate of fuel MTBE and other gasoline-related compounds from rivers and streams. Pankow (10) and Rathbun (7) procedures were used in this study for the estimation of the vaporization rates for ETBE under similar conditions. Modeling results show that volatilization rate for MTBE and ETBE from flowing surface waters depends on depth, velocity of flow, and ambient temperature. In general, increasing the flow depth and decreasing the stream velocity both increase the half-life of organic solute in the stream. Modeling results show that in deep and slow-moving flows, MTBE and ETBE volatilize at rates which are similar to those for the BTEX compounds. In shallow and fast-moving flows, MTBE volatilizes at rates that are significantly less than those for BTEX compounds. In shallow and fast moving streams, ETBE vaporization is much faster than MTBE but lower than BTEX compounds. A summary of the results is presented in the experimental section.

Remediation Technologies

MTBE's high solubility in water, low rate of adsorption to soil, and low biodegradation can complicate the treatment of groundwater contaminated with MTBE and make it more expensive than groundwater contaminated with petroleum that does not contain MTBE (11). There have been several evaluations of remedial technologies for MTBE, but these have generally indicated low efficiency and high costs for the technologies. For example Garrett and co-workers (12) concluded that filtration of MTBE-contaminated ground water through activated carbon was not cost-effective

Remediation technologies were evaluated by Butillo *et al.*, (13) for the treatment of MTBE in water from petroleum storage facilities. Air stripper packed column heights were compared to air stripping at elevated temperatures. Removal of 99.41, 99.78 and 100.00% of MTBE at 65, 80 and 100 F was predicted. Butillo and co-workers (13) also completed the engineering design of a water treatment system. In this system, the effect of water temperature on the removal efficiency of MTBE was studied. Laboratory analytical results of effluent water samples indicated a removal efficiency of 99.98% for MTBE and BTEX compounds from the water stream.

Truong and Parmele (14) studied eight different treatment technologies for the removal of MTBE from water. This study was conducted by TRC Corporation for the American Petroleum Institute. The treatment methods were: air stripping with aqueous-phase carbon adsorption, air stripping with heated air stripping, steam stripping, diffused aviation, above ground biological treatment and UV catalyzed oxidation using hydrogen peroxide and ozone. The cost per 1000 gallons of water treated ran from $9 to $23, with air stripping being the overall cheapest, and steam stripping or above ground biological treatment being the most expensive.

In a study by Johnson (15), theoretical analysis of the mechanism and factors contributing to the overall performance of in situ air sparging systems for the removal of oxygenates such as MTBE is presented. In this study the significance of volatilization, biodegradation, bulk water flow, chemical concentrations, partitioning parameters, and air distribution is evaluated. The analysis indicated that in situ air sparging has significant potential for remediating spills of very soluble, but slowly degradable fuel oxygenates, such as MTBE and ETBE.

Use of highly crosslinked polystyrene for the adsorption of MTBE from groundwater or wastewater has been recently proposed by Ameripure, an environmental company in Bakersfield, California. (16). It is claimed that the polystyrene at $30/lb may be regenerated with steam for reuse.

Blending Properties of Gasoline with MTBE and ETBE

Vapor Pressure

Furey and Perry (17) have reported 4.3 and 4.6 psi for the Reid vapor pressure (Rvp) of ETBE. Also, Rvp of 4.0 and 4.4 psi are reported by Brockwell *et al.*, (18) and Shiblom *et al.*, (19), respectively. The reported values of Rvp for ETBE are all considerably lower than the Rvp of about 8.0-psi, which has been reported for MTBE (18).

The blending Rvp of a compound in the fuel is a very important factor which effects the environmental impact due to its vaporization. In contrast to a slight increase in Rvp which occurs when MTBE is added to gasoline (18), the addition of ETBE results in lower Rvp than the corresponding gasoline and the decrease in Rvp almost linearly continues with the increase in the concentration of ETBE in the blend. In a study by Shiblom *et al.*, (11) for Phillips Petroleum Company it is documented that at 2.0 wt% oxygen level with ETBE, the RVP was lowered by about 0.6-psi compared to the base gasoline and at an oxygen level of 3.7 wt% the difference was about 1.3-psi. In contrast, at 2.0 wt% oxygen level with MTBE there was no change in the RVP of the blend compared to the base gasoline and at 3.7 wt% a 0.2 psi increase was reported. It can be seen that ETBE has a vapor pressure advantage over MTBE, which is of considerable importance due to the ever-lowering limits on RVP because of air quality considerations. Lower Rvp also will allow for more butane in gasoline, a desirable blend stock, without Rvp penalty.

Research and Motor Octane Numbers

The output of an engine is determined by its knocking. Octane numbers provide a measure of a gasoline's ability to resist engine knock. Oxygenated blending agents for gasoline such as ethanol, MTBE, ETBE and TAME posses excellent octane enhancement properties (4). Shiblom and co-workers (19) have documented the enhancement in the Research and Motor Octane Numbers (RON and MON) at three blending oxygen levels of 2.0, 2.7 and 3.7% for MTBE and ETBE. Results showed a significantly higher RON and MON for ETBE compared with MTBE. For example, at 2.7% oxygen content, ETBE had a RON and MON boost of 4.65 and 3.43, respectively, when compared with base gasolines of 92.0 RON and 83.9 MON. At the same oxygen level, the boost for MTBE was 3.10 and 2.37 for ROM and MON, respectively.

Oxygen Content

The Clean Air Act Amendments of 1990 set minimum oxygen content of 2.0 wt% for reformulated gasoline in ozone non-attainment areas. ETBE has a lower oxygen (15.7 wt%) than MTBE (18.2 wt%). Therefore, to achieve a 2.0 wt% oxygen in gasoline, 12.8 vol% ETBE should be added to gasoline, while it takes only 11.0 vol% of MTBE to reach the same level of oxygen in gasoline for a difference of 1.8 vol%. To reach higher levels of oxygen this difference will become even larger. Therefore, because more ETBE is needed to meet a certain level of oxygen, it also dilutes more of the other components targeted for reduction in the gasoline stream, including aromatics, sulfur, olefins, and benzene, providing an option for refiners to avoid installation of more costly refinery upgrades.

Material Compatibility

Ether blended gasolines have been thoroughly investigated for material compatibility and in general no considerable detrimental effects have been reported on the components of the fuel system. In older vehicles higher rates of deterioration of elastomeric materials have been reported (20). However, new elastomers called fluoroelastomers, which have been used in automotive engines since the mid-1980's are specifically designed to handle all modern gasolines, including high ether-containing, ethanol-containing, and high-aromatic gasolines without experiencing any detrimental effects. Fluoroelastomers are far more resistant to permeation and corrosion than were earlier elastomers (4).

Permeation studies by Shiblom and co-workers (19), on the fuel dispenser hose, hydraulic hose, and neoprene fuel lines with 11.8 and 23.5 vol% ETBE blends resulted in satisfactory permeation rates. Also, the swelling of polymeric and elastomertic parts was shown to be no greater than typical gasolines and no considerable corrosion of metallic components were reported.

Experimental Studies

The focus of the experimental investigations was to compare the volatility and ease of separation of ETBE and MTBE from water. One set of experiments simulated the volatilization of ethers from flowing surface water (for example, rivers and streams) and from a quiescent source (for example, lakes and ponds). A second set of experiments examined air stripping and activated carbon

adsorption for the removal of ethers from water. Experiments were also performed to determine the solubility of the ethers in water and their tendency for separation in the presence of water in gasoline.

Materials

MTBE (98%,) was obtained from Aldrich Chemical Company. ETBE was provided by ARCO Chemical Company. Methanol was obtained from Fisher Scientific. Distilled water was used in all of the experiments. Granulated charcoal was 4-8 mesh and was obtained from Sigma Chemical Company.

Analysis

A Hewlett-Packard HP-6890 series GC system equipped with an HP-5 capillary column (21 m × 0.32 mm ID × 0.17 μm), HP Series II GC Electronic Pressure Control, and split-splitless inlet was used for the analysis. The inlet was operated in the split mode with a split ratio of 15:1. Inlet temperature was maintained at 325 °C at a pressure of 30.4 psi. The column was operated in constant flow mode. The oven initial temperature was 50 °C and held at this temperature for 0.5 min. The oven was then ramped to 200 °C, at 35 °C per min. The oven was held at this temperature for 0.93 min to complete the run. The overall run time for this method was 5.72 min. The GC was equipped with flame ionization detector. The detector was held at 350 °C with a Hydrogen flow of 30-mL/min, an air flow of 275 mL/min., and a helium flow of 21 mL/min.. Internal standard procedure was used for the calibration. Each sample was analyzed three times and an average value was used in the calibration chart.

Volatilization from Water

In this section, the modeling results for the volatilization of MTBE, ETBE, and benzene are presented first. Experimental studies are presented later and were designed to verify the accuracy of the modeling results.

As was mentioned earlier, Pankow et al., (10) studied the volatilization of MTBE and benzene, a representative of the BTEX group. Based on the two-film theory of diffusion, volatilization rates were estimated as a function of the mean flow velocity, the mean flow depth, the ambient temperature, and the wind speed. Two temperatures (winter, 5 C, and summer 25 C), two wind

speeds (calm 0.25 m/s, and windy 5.5 m/s), five stream flow velocities (0.32, 0.100, 0.316, 1.000, and 3.162 m/s), and five flow depths (0.1, 0.3, 1.0, 3.2, and 10.0 m) were considered. Volatilization rate was based on the time required for the organic solute to reach half of its original concentration ($t_{1/2}$ = half-life).

At both 5 and 25 C, for deep and slow-moving flows, there were only small differences in the $t_{1/2}$ values between the calm and windy conditions. For example, at 5 C for a 10-m deep flow and 0.032 m/s of flow velocity, $t_{1/2}$ was 85.3 and 78.2 days for MTBE under calm and windy conditions, respectively. The corresponding values were 82.2 and 80.4 days for ETBE, and 68.2 and 68.0 days for benzene, under calm and windy conditions, respectively. This is due to the fact that MTBE, ETBE and benzene are all sufficiently volatile from water (*i.e.,* Henry's law constant are large enough) that under these conditions, the overall mass transfer process is controlled largely by transport on the liquid side. And for all practical purposes the evaporation rates for MTBE and ETBE are identical and not much slower than benzene. Moreover, while changing the flow depth and velocity affect $t_{1/2}$, increasing wind speed has relatively little effect. The same conclusion applies at 25 C.

At both 5 and 25 C, for shallow, fast-moving flows, the situation is largely reversed so that changing from calm to windy conditions provides a significant acceleration in the volatilization rate. For example, at 5 C for a 0.1 m deep flow and 3.162 m/s of flow velocity, $t_{1/2}$ was 0.1013 and 0.0310 days for MTBE under calm and windy conditions, respectively. The corresponding values for ETBE were 0.0312 and 0.0138 days, and for benzene were 0.0102 and 0.0076 days, for calm and windy conditions, respectively. As regards to shallow, fast moving flows, the evaporation rate is about 3.2 to 2.2 times faster for ETBE than MTBE under calm and windy conditions, respectively. Similar large differences were evident at 25 C.

Volatilization from a Flowing Stream

The first setting was a simulation of a flowing stream of water in a rectangular trough. The trough was 40 inches long and 7.5 cm wide and could hold up to 6 cm of water. Initially, a fixed amount of water-ether mixture (7.5 L) with a certain initial concentration of ether was charged into the sealed water tank. Water/ether mixture was pumped into the trough reservoir by a 1.1 amp submerged pump, which was placed in the water tank. Water-ether mixture was then allowed to flow over the trough and back into the reservoir. The water level on the trough was controlled with the aid of two valves, which were installed at the outlet of the pump and the trough. Water was drained back into the water reservoir and recirculated over the trough. Water flow rate was

set at 2.4 L/min. At this flow rate the water height was maintained at 5 cm in the trough. Samples were taken over an 8-hour period to monitor the concentration of the ethers in water.

In the initial experiment the concentration of ethers was at approximately 0.40 wt%. Results for the first 8-h of these experiments are summarized in Figure 1. This figure shows that the rate of dispersion of the ethers from water was similar. No significant differences between the dispersion rate of the two ethers were observed. No measurable amount of ethers was detected after 22 hours.

Dispersion from a Stirred Tank

The trough experimental setup had little flexibility when a variation in experimental settings was needed. The water height on the trough and its flow rate were both at the low end for simulating a flowing stream and as was demonstrated in the previous section, under these conditions no significant differences were observed between the ethers. To explore the differences between the ethers it was necessary to operate the trough experiment at higher water flow rates. Due to the limitations of the experimental setup, it was not possible to maintain steady state operation at higher water flow rates. This was particularly difficult for long run times (12-24 h).

To further investigate the dispersion of ethers from water a stirred tank was used. In a stirred tank, the water-air interaction can be changed by simply varying the stirring rate and the stirring condition could be maintained for long periods of time with no difficulty. A 4.5-L container was used for this experiment. The container was 17 cm in diameter with a height of 18cm. A Stedfast Model SL1200 mechanical stirrer was used for stirring. The stirrer had swivel type impellers, which were 1.25 cm long. The depth of the stirrers seemed to play an important role on the rate of dispersion. The ethers dispersed much faster if the stirrer caused bubbles in the buckets. This was prevented by immersing the impeller 10-cm below the surface.

The bucket was initially charged with 4 L of a known water/ether solution. The initial concentration of ethers was at 1.0, 0.5 or 0.4 wt%. Samples were collected over a 24-h. The stirrer speed was set at 480, and 1100 rpm for low and high mixing intensity experiments, respectively. The temperature of the water/ether mixture was at room temperature (22 C).

A representative sample of the experimental results is presented in Figure 2. As this figure shows, ETBE was dispersed at a slightly faster rate but no significant differences were evident between the two ethers.
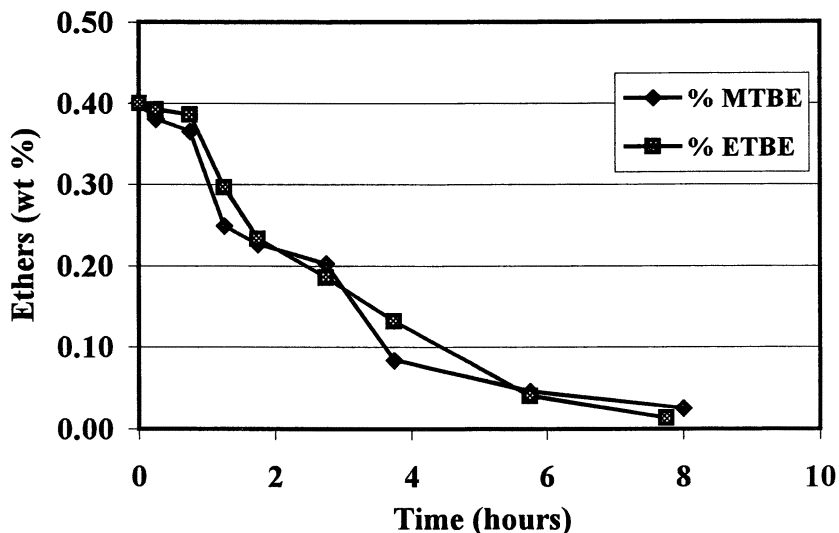
Figure 1. Rate of dispersion of MTBE and ETBE from water in a trough setting subject to an initial ether concerntration of 0.4 wt%.
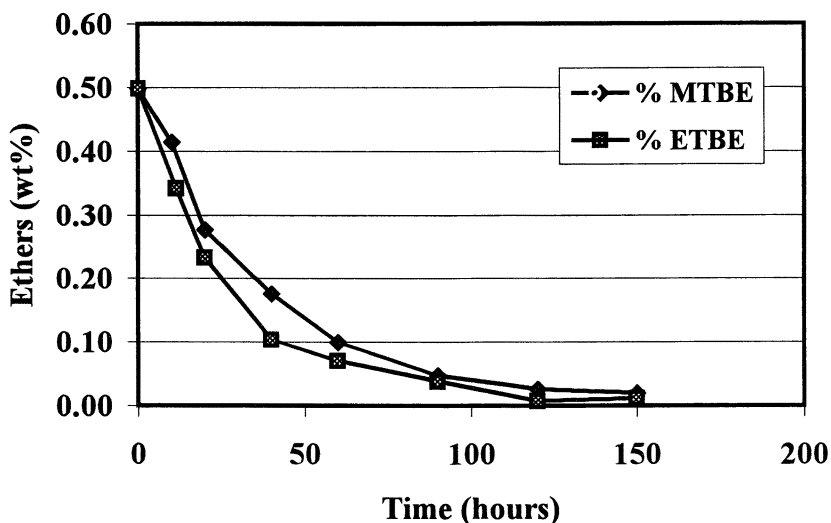
Figure 2. Rate of dispersion of MTBE and ETBE from water in a very high-stirred tank subject to an initial ether concentratio of 0.50 wt%.

Remediation of MTBE and ETBE Contaminated Water

Two treatment technologies were evaluated for the removal of ethers from water in this study. The first method was an air stripping (desorption) in a packed bed and the second method was absorption by activated carbon in a fixed bed.

Air Stripping

Air stripping was evaluated for the removal of MTBE and ETBE from water. A glass column, which was 32 inches long and 3 inches in diameter, was used in this experiment. The column was packed with ceramic rings. The packing height was 24 in. A liquid distributor was installed at the top of the column to evenly distribute the liquid over the packing material and to minimize the potential for channeling. Water with a certain initial concentration of ether was pumped from a closed reservoir tank to the top of the column and was recovered into the same reservoir tank after passing through the column. Liquid flow rate was at 6.6 L/min for all experiments. At this flow rate no flooding was experienced in the column. Air flowed counter currently from the bottom of the column and was controlled and measured by an air flow meter. A constant-temperature circulating bath (VWR Scientific Model No. 1157) regulated the temperature of the liquid by circulating water through a copper coil inside the reservoir tank. All the experiments were performed with an initial ether concentration of 0.5 wt%. Samples were collected from the water reservoir tank over a 2-3 hour period. The effects of air flow rate and water/ether temperature on the rate of removal of the ethers from water were evaluated in these experiments.

The effect of air flow rate was examined in the first set of experiments. Experiments were performed at the air flow rates of 5,10, 20, 25, and 80 cubic feet per hour (CFH) and at a constant temperature of 20 C. Results for these experiments are presented in Figures 3 and 4 for MTBE and ETBE, respectively. In these figures, variations in the concentration of the ethers is plotted as a function of time. As these figures show, the rate of removal of the ethers from water is directly proportional to the flow rate of air through the column. These figures also indicate a much faster rate of removal for ETBE compared with MTBE. At the relatively high air flow rate of 80 CFH the rate of desorption of both ethers is quite fast; however, it was much faster for ETBE. For example, at 80 CFH after about 30 minutes, no measurable amount of ETBE was detected in the samples, whereas, for MTBE a measurable 0.0016 wt% was detected after 60 minutes of stripping. At the slower airflow rate of 25 CFH, the differences between the rate of desorption of the two ethers is more
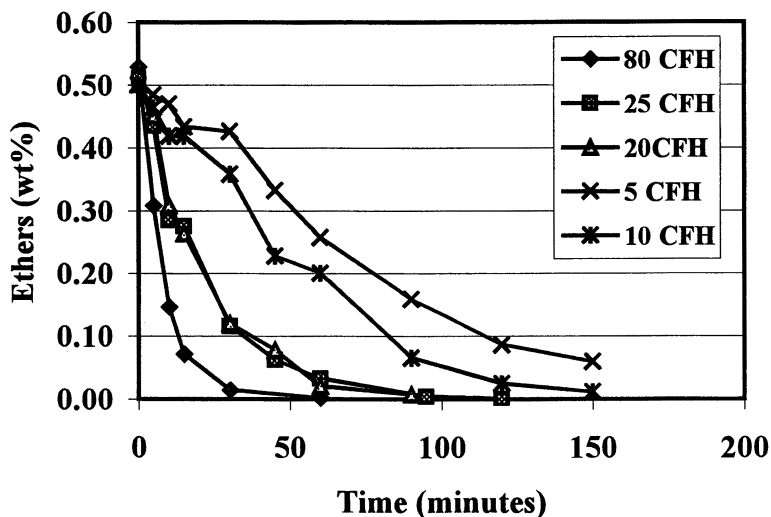
Figure 3. Rate of stripping of MTBE from water in a packed column subject to an airflow rate of 5,10, 20, 25, and 80 CFH.
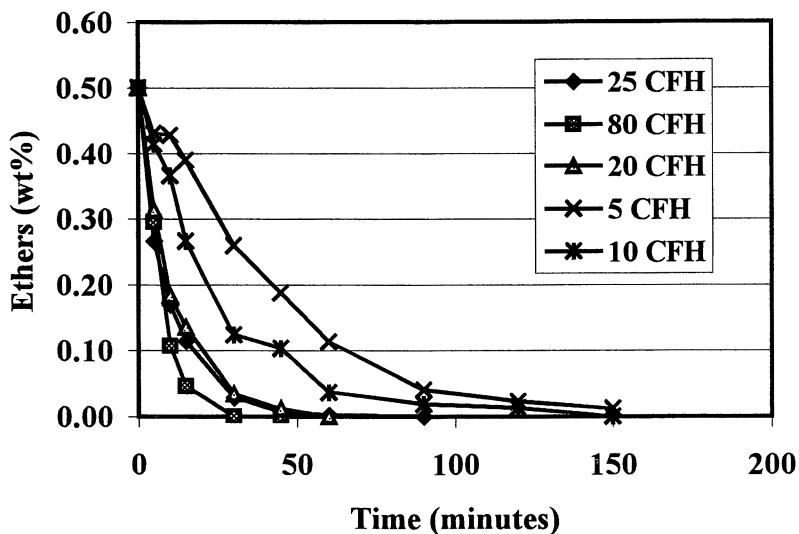
Figure 4. Rate of stripping of ETBE from water in a packed column subject to an airflow rate of 5, 10, 20, 25, and 80 CFH.

significant. For example, at 25 CFH the half life of MTBE was about 17.5 min compared to about 6 min for ETBE.

The second set of experiments explored the effect of temperature on the rate of desorption of ethers from water. Experiments were performed at a constant air flow rate of 10 CFH, while the temperature of the water/ether mixture in the reservoir tank was at 10, 20, 30, 40, and 50 C. Results for these experiments are presented in Figures 5 and 6 for MTBE and ETBE, respectively. As these figures show, the rate of removal of the ethers from water is directly proportional to the temperature of the water/ether mixture in the reservoir tank. These figures also indicate a much faster rate of removal for ETBE compared with MTBE.

Activated Carbon Adsorption

A fixed-bed activated carbon adsorption column was used as a stand-alone separation device in the experimental studies. The adsorption column was packed with activated carbon. The height of activated carbon in the column was 23 in. Activated carbon used in the experiments was 4-8 mesh untreated granular. The initial charge to the reservoir tank was 4 L. Samples were collected from the water reservoir tank over a two-hour period.

Experiments were performed with an initial ether concentration of 0.50 wt%. The experimental results for the rate of removal of ETBE and MTBE during the course of adsorption are summarized in Figure 7. As this figure shows, the rate of adsorption of ETBE on activated carbon was much faster than MTBE. The amount of MTBE, which was detected in the sample after 2 hours of adsorption, was about 0.0218 wt%. To reach a similar level in ETBE only 45 minutes of adsorption was required. The ETBE level after 2 hours was measured at 0.0069 wt%, which was significantly lower than the MTBE level after 2 hours.

Solubility of MTBE and ETBE in Water

The solubility of MTBE and ETBE were measured at 72 F, which was the room temperature at the time of the measurement. In a vial which was initially charged with distilled water, MTBE or ETBE in excess of what was possibly soluble in the water, was added. The addition of ethers was gradual and in several increments, and each increment was followed by vigorous mixing to ensure maximum solubility. Due to the limited solubility of the ethers, after the maximum solubility of ethers was reached, a second insoluble ether-rich phase was formed on the top of the water-rich phase. The two phases were then allowed to completely separate and equilibrate. The water-rich phase was analyzed by GC to determine the solubility of the ethers in water. The solubility
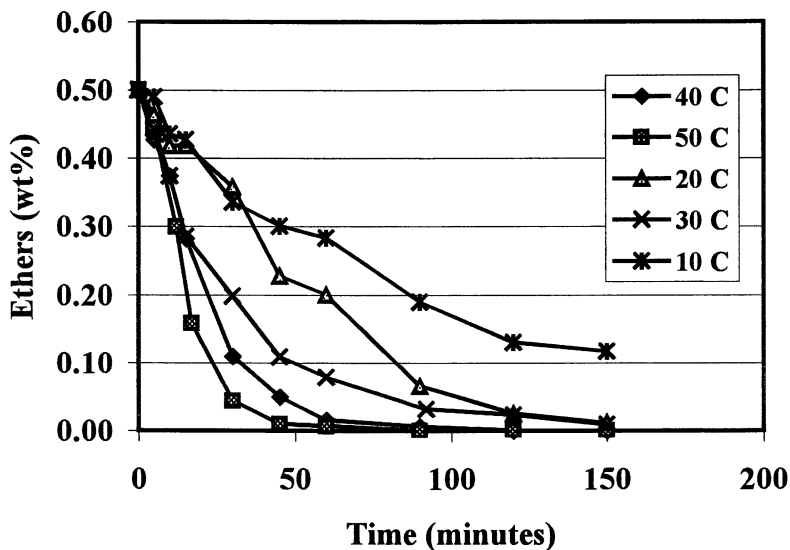
Figure 5. Rate of stripping of MTBE from water in a packed column subject to an airflow rate of 10 CFH and 10, 20, 30, 40, and 50 C.
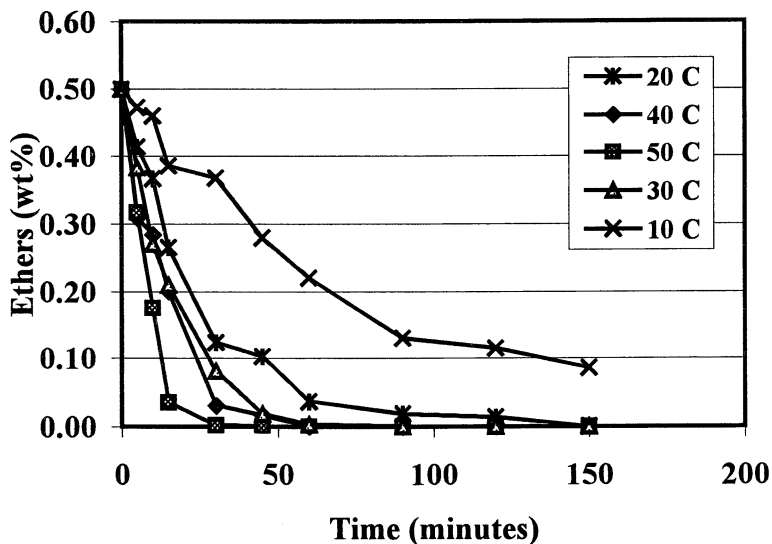
Figure 6. Rate of stripping of ETBE from water in a packed column subject to an airflow rate of 10 CFH at 10, 20, 30, 40 and 50 C.
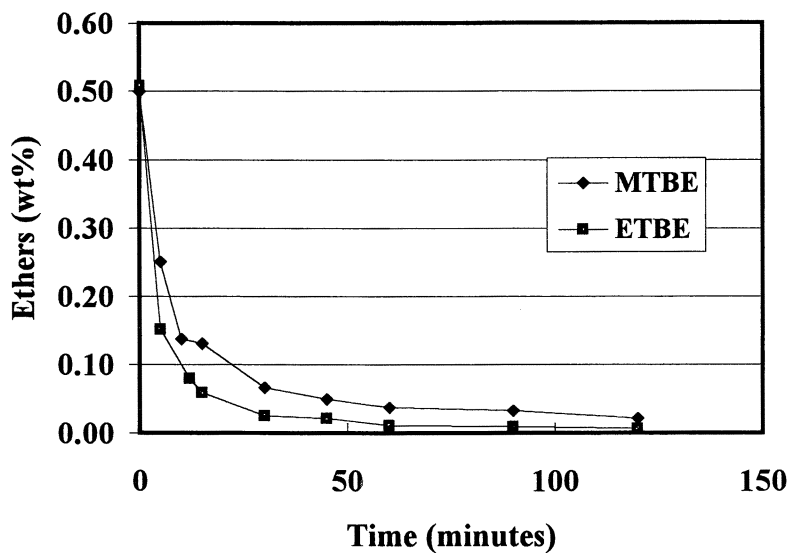
Figure 7. Rate of adsorption of MTBE and ETBE on activated carbon subject to an initial ether concentration of 0.50 wt%.

of MTBE at the lab temperature of 72 F was 3.85 wt%. Under the same conditions the solubility of ETBE was 1.10 wt%.

Phase Separation of Gasoline-MTBE and ETBE Blends

Phase behavior of gasoline/ether blends in the presence of water was investigated. Experiments were performed to measure the amount of ether that extracts from a gasoline/ether blend to the aqueous phase. Vials were initially charged with 10 mL (7.22 g) of ether/gasoline blends. Blends were all 15 % ether by volume (6.11 g water and 1.11 g ether). Then, 500, 1000, and 1500 μL of water were added to each vial. After vigorous mixing, the two phases were allowed to completely separate and equilibrate. The water-rich phase was analyzed by GC to determine the amount of ether that was extracted from the gasoline-rich phase. Results indicated a lower amount of ethers extracted from the gasoline blend for ETBE compared to MTBE. However, in both cases, the extracted amount was relatively small and only 0.14 and 0.18 wt % of the initial ether in the gasoline was extracted for ETBE and MTBE, respectively.

Discussion of Experimental Results

Experiments were designed to simulate the natural dispersion and volatilization of MTBE and ETBE from a flowing stream or quiescent (pond, lake, etc) setting. Experiments under low water-air interaction (no mixing) did not reveal a significant difference in the rate of dispersion of the two ethers. In these experiments, under low to moderate water-air interactions (low mixing), ETBE showed a slightly faster rate of volatilization from water compared to MTBE. This behavior is due to the limitations by the liquid side and no significant effect from the Henry's Gas Law Constant (HGC) is evident in the overall transport. This was also consistent with the modeling results, which predicted very little or no appreciable differences between the volatilization rate of ETBE and MTBE.

Under moderate to high water-air interactions, there was a significantly faster volatilization rate for ETBE compared to MTBE. This is due to the fact that, under these conditions the gas and liquid transport coefficient both contribute to the overall mass transfer coefficient which means more contribution from HGC. The larger value of HGC for ETBE becomes the determining factor in the rate volatilization rate.

Air stripping in a packed column under a variety of conditions for temperature and airflow rate was investigated for the removal of MTBE and

ETBE from water. Fundamentally, air stripping is to create a very high interaction between the gas and liquid phases. Therefore, with respect to the volatilization experiments, air stripping should be considered as moderately high to very high as far as the liquid-gas interaction is concerned. Under a certain liquid flow velocity, the gas flow velocity will determine the degree of interaction between the two phases. At lower gas flow rates, there will be contributions from both phases to the overall mass transfer coefficient and larger values of HGC dominate the overall mass transfer coefficient. As the gas flow rate is increased, eventually, the liquid phase transport coefficient becomes the limiting coefficient and the contribution of HGC becomes minimal. Experimental results were consistent with this behavior. There was a distinct difference between the rate of dispersion of ETBE and MTBE at lower air flow rates. This difference became insignificant at very high air flow rates.

Adsorption with activated carbon was very effective in the initial removal of MTBE and ETBE from water. The rate of adsorption of ETBE on activated carbon was much faster than MTBE. A slight amount of ethers did remain in the samples which was verified to be as a result of an equilibrium condition for ethers between the liquid and solid phases. From an operational viewpoint, activated carbon adsorption stays a viable alternative due to the ease of processing and handling of the removed ethers and also for small operations such as residential applications.

Phase behavior studies of gasoline-ether blends in the presence of water did not show any tendency for the transport of ethers to the water phase and minimal amount of ether was extracted from the gasoline. The amount of ethers that was extracted from the gasoline blend was lower for ETBE compared to MTBE. The lower solubility of ETBE in water may have been responsible for this behavior

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Beyond Methyl *tert*-Butyl Ether: Applying the Precautionary Principle to Gasoline Oxygenates

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Based on an evaluation of the physicochemical and toxicological properties of Methyl tert-Butyl Ether (MTBE), as well as an ex post-facto cost and benefit analysis, it has become clear that there are less expensive and disruptive approaches to achieving the goals of the 1990 Clean Air Act Amendments with regards to gasoline-powered mobile sources. However, before jumping to the next blending component to improve combustion efficiency and reduce air emissions, we propose a thorough investigation of the properties of alternatives to MTBE, such as ethanol, toluene or alkylates. We conducted a preliminary cost/benefit analysis of the various alternative formulations based on the information available in California. We conclude that non-oxygenated reformulated gasoline presents the least cost for the same benefits. However, we should apply the Precautionary Principle and conduct an exhaustive research program to ensure that such widely used gasoline components are not persistent and that the toxicological or organoleptic properties are within acceptable bounds.

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Introduction

It has often been said that if gasoline had recently been invented, it could not obtain approval for today's marketplace, given its toxicological properties. For most human beings, gasoline is one of the chemical mixtures to which they will most likely be exposed in significant amounts throughout their lifetimes. Since gasoline includes benzene and other aromatic compounds, it would be classified as a carcinogenic substance. In addition, given that the intended use is to combust gasoline for fuel, there would be significant concern with the known generation of hundreds of products of incomplete combustion, including aldehydes, carbon monoxide and many other potentially toxic organic compounds, as well as nitrogen oxides. After more than 100 years of use, gasoline continues to generate significant controversy, as the recent experience with Methyl tert-Butyl Ether (MTBE) indicates.

In addition to the toxicity of some gasoline components, the introduction of gasoline additives to improve the performance of the internal combustion engine continues to present challenges. Adding compounds to gasoline to improve performance dates back almost 80 years, starting with the introduction of tetraethyl lead (TEL) to gasoline to reduced engine "knock" by improving the octane rating. Despite the fact that as early as the 1920s public health experts, government officials and many other people were acutely aware of the dangers posed by the introduction of lead into gasoline (1,2), TEL was added for over 60 years in the US, and continues to be used in many countries around the world, for economic considerations. In the early 1970s, gasoline producers began to feel the pressure to find substitutes for TEL. Industry studies as early as the 1950s indicated that several ethers, including MTBE and Ethyl tert-Butyl Ether (ETBE), could improve the octane ratings of a gasoline mixture. Since MTBE could be produced from isobutylene, a refining byproduct, it was a logical choice. As TEL was phased out, MTBE began to be widely used at 2 to 3 % by volume.

Studies by the automobile and oil industry indicated that the use of these ethers could significantly improve the combustion of gasoline, reducing carbon monoxide emissions (3). Preliminary results from these studies led to the incorporation of an "oxygen-content" mandate in the 1990 Clean Air Act Amendments (CAAA), for reformulated gasoline sold in areas where air quality standards were not being met. A number of other specific requirements were imposed on the new gasoline formulations; rather than specify performance requirements, legislators decided to dictate the way gasoline should be produced. For the most part, gasoline producers decided to use MTBE, since it provided the required oxygen content, and was in general easier to blend with gasoline than ethanol. In addition, MTBE was cheaper than ethanol in most regions, and

the supply was not dependent on agricultural prices and other issues concerning the ethanol market. In several mid-western states gasoline was blended with ethanol to produce "gasohol" and meet the oxygen content requirements.

At the time all these decisions were being made, the toxicological information on MTBE and other potential "oxygenates" was incomplete. The fate and transport data indicated that these compounds would be rather soluble in water, with little sorption, indicating that if any MTBE or other oxygenates leaked from Underground Storage Tanks (USTs), they could potentially travel far towards drinking water wells. Information on their natural rate of biodegradation was practically non-existent. One would assume that this would have led regulators to immediately start a major research effort to collect such data (toxicity and biodegradability), but since the main concern was air quality, potential impacts on water resources did not become prominent. Once again, economic considerations came first, without a full consideration of the entire life cycle of these oxygenates.

MTBE began to make headlines once prominent leaks in the City of Santa Monica, CA resulted in the shut down of several drinking water supply wells, with a potential liability to the responsible parties of millions of dollars (4). Once it became common place to include MTBE in the analysis of contamination around USTs as well as surface water reservoirs where motor boats are allowed, it became clear that MTBE contamination was much more widely spread than regulators had foreseen. In a very short time, MTBE began to be detected in hundreds and then thousands of wells around the US, wherever it had been used since the phase-out of TEL. California legislators passed California Senate Bill 521, which mandated a thorough review of the health and environmental impacts of MTBE in the state, to be conducted by the University of California. The report produced a truly interdisciplinary, multimedia evaluation of the impact of MTBE (5), including a cost-benefit analysis that clearly indicated that there were cheaper alternatives to obtain the air quality objectives of the 1990 CAAA (6). Based on these findings, Governor Gray Davis decided to phase out the use of MTBE in California over the next three years (7). USEPA has recently given "Advance Notice of Proposed Rulemaking to Control MTBE in Gasoline", which sends a clear signal about its position on MTBE (8).

Several alternative blending components have been identified for MTBE, including ethanol, toluene and alkylates (6,9-11). We are again at a crossroads where important decisions will be made on chemicals that will be widely used, and it would seem that the use of the precautionary principle is appropriate. This study thus presents a review of the most relevant considerations regarding these

various gasoline formulations, and discusses the issues that should be evaluated *before* another costly mistake is made. We limit our scope to gasoline formulations, but clearly the precautionary principle could be applied more generally to the use of gasoline.

Precautionary Principle

The precautionary principle was first applied internationally in the context of marine pollution control, through the 1987 Declaration of the Third Ministerial Conference on the North Sea as "action to avoid potentially damaging impacts of substances that are persistent, toxic and liable to bioaccumulate" (12). Behind every major environmental policy decision there is an element of scientific uncertainty. The Bergen Declaration clearly states that policy making should not be postponed due to incomplete information when there is sufficient reason to believe that preventive action might diminish environmental impacts (13). Part of the preventive measures that should be taken immediately is a full cross-media assessment of environmental impacts, and a determination of scientific uncertainties. Research to reduce these uncertainties should be an integral component of any new legislation that involves substances that are persistent, toxic, can bioaccumulate and are produced in large quantities. Any substance added to gasoline in a significant amount should be fully characterized with respect to its persistence, toxicity and bioaccumulation, since it is a given that it will be produced and distributed in large amounts. Failure on any count should be a reason for searching for alternatives.

On practical terms, it is not feasible to demand that companies demonstrate that every substance is absolutely harmless. However, certain rules should be established based on sound scientific methods that relate chemical structure to activity (e.g. hydrophobicity, biodegradability, toxicity). Good science involves raising a yellow flag when it is probable that a new substance is likely to produce a bad outcome, and this should be followed through with an aggressive research effort to make sure that all the environmental impacts have been assessed. The increasing liability issues raised by these substances should lead firms to apply the Precautionary Principle as part of a "Best Management Practice".

In the next section, we present the results of our cost-benefit analysis for different gasoline formulations across all environmental media, which emphasizes the need to apply the Precautionary Principle for the next generation of gasoline blending components.

Analysis Costs and Benefits of Gasoline Formulations

The following study of the costs and benefits of three gasoline formulations that meet California's Phase II Reformulated Gasoline (CaRFG2) requirements was conducted in 1998, after CaRFG2 with MTBE had been in the California market for over two years. The study included CaRFG2 with ethanol and non-oxygenated CaRFG2. An important component of our analysis was to keep track of our uncertainties, and to make sure that the final answers (net cost or net benefit) reflected such uncertainty. Thus, if a proposed alternative results in a net cost, even when all the uncertainties are considered, the Precautionary Principle indicates that research to reduce the uncertainties should be started immediately, and the implementation of the alternative should be contingent on a new outcome (i.e. a net benefit).

The study was focused on California due to the funding source, but can be easily generalized to all those areas (US or around the world) where MTBE is being used or is under consideration. There will be some differences, given the diversity of opinions on the level at which water contaminated with MTBE should be treated (which has a major impact on the overall cost of treatment). In addition, the air quality benefits may differ, depending on the level of air pollution. In addition, the uncertainties regarding the prices of the various blending components (MTBE, ethanol, toluene, alkylates) will become greater in the short-term if many regions switch to these compounds. It should be noted that without having done a full analysis, clearly the substitution of TEL by MTBE has produced major health benefits around the world, although it is probable that the same benefits would have been realized with alternative formulations that did not adversely affect water quality.

All costs and benefits for the different gasoline formulations evaluated are estimated relative to conventional gasoline, the typical gasoline formulation sold before the implementation of the 1990 CAAA. To simplify the analysis, we assume that each gasoline alternative is used 100% in California.

Air Quality Benefits

For the air quality benefits, we considered the reduction in benzene and other air toxics concentrations in the atmosphere, as well as the projected decrease in carbon monoxide and ozone concentrations from the cleaner burning reformulated gasoline. The health benefits are essentially the same across all three formulations, since studies have shown that all these formulations achieve essentially the same carbon monoxide and ozone precursors emissions reductions, within statistical significance. To derive a value of air quality

benefits associated with reduced morbidity effects from decreases in carbon monoxide and ozone we used the cost of illness approach which sums medical expenditures and lost wages associated with morbidity. The total value of benefits from avoiding morbidity due to carbon monoxide is the sum of hospital and restricted days avoided which equals $9.6 million. The total value of benefits from avoiding morbidity due to ozone is the sum of hospital days and restricted days avoided which equal $8.8 million. Ambient concentrations may vary widely, spatially and temporally, even within an air basin. To simplify our analysis, we assumed that the 1-hr average ozone concentration was uniformly distributed, which may result in an overestimate of the benefits, since a smaller subset of the population is experiencing the higher concentrations.We provide a detailed accounting of our calculations in (6) and (14).

As air quality improves, the impact of reformulated gasoline such as CaRFG2 on ambient air quality will decrease, when measured in absolute terms. For example, by the year 2000, the decrease in benzene concentrations is estimated to be only 0.03 to 0.08 ppb; the reduction in cancer risk will be much smaller than at the introduction of CaRFG2. We therefore expect the human health benefits of CaRFG2 to decrease over the next few years. It is also important to consider the decreases in human health benefits of MTBE or oxygenates due to changes in the emissions control technology of the vehicle fleet. Thus, the benefits of adding oxygenate to gasoline formulations are relatively small and decreasing with time and may result in health costs from combustion byproducts (e.g. formaldehyde).

Air Quality Costs

The combustion of MTBE results in a slight increase in the concentration of formaldehyde in the vehicle emissions, due to incomplete combustion (9,15). Combustion of ethanol produces increases in acetaldehyde (9). Both of these aldehydes are known carcinogens. While the air quality costs for MTBE may range from $0 to $27 million, the uncertainty in the magnitude of acetaldehyde emissions from ethanol combustion produces a cost estimate of $3 to $200 million. Since gasoline/ethanol formulations have been sold in the Midwestern USA and in Brazil for several years, it should be rather inexpensive to reduce the uncertainty in this cost estimate by collecting data at these locations.

Combustion of additional toluene or alkylates has not been shown to significantly increase the emissions of air toxics, but it should be pointed out that the studies have been limited and that additional work is needed to reduce the uncertainty in this respect.

Water Quality Costs

The annualized cost (i.e. total cost divided by the number of years considered for treatment) of treating MTBE-contaminated surface and ground waters in California was estimated in 1998 to be on the order of $340 to $1,480 million per year, relative to the cost that would have been incurred if conventional gasoline had been used. The major treatment cost is the clean-up of Underground Storage Tank (UST) leaks, which is expected to cost from $327 to $1,400 million, above the cost that would have been incurred if conventional gasoline without MTBE had been used. If the UST technology and workmanship could deliver 100% leak proof tanks, the savings and reduced environmental impact would be considerable. The estimates on the number of tanks that have leaked gasoline with MTBE were obtained from (16) and (17). Unit water treatment costs were prepared based on experimental studies (18). Groundwater remediation costs include the legacy of older leaking USTs in California that stored gasoline with MTBE, which will cost from $320 to $1,030 million per year to remediate in the next few years. The projected cost of future leaks of MTBE from upgraded USTs is between $7 million and $370 million, with a large uncertainty about the effectiveness of new upgraded tanks.

Since ethanol biodegrades fairly rapidly, it would appear that the cost of using ethanol, in terms of risk to the water supplies, is low. Recent studies (19,20) indicate that the rapid biodegradation of ethanol at the leading edge of a groundwater plume would deplete dissolved oxygen. This in turn will result in an extension of the BTEX plume of up to 30%, which might result in a larger number of BTEX plumes reaching drinking water wells. The organoleptic properties of water with low concentrations of ethanol have not been determined, and while some might not perceive ethanol at low concentrations, others might find it unacceptable in their drinking water supply. The uncertainty resulting from these considerations has not been included in our analysis, but should be a priority research area if ethanol is considered as an MTBE replacement.

For non-oxygenated gasoline, the differential cost of remediation and/or water treatment relative to conventional gasoline is small. The increased volumetric fraction of toluene in non-oxygenated CaRFG2 will result in higher initial toluene concentrations, but toluene is easily biodegraded by the intrinsic microbial communities. Treatment technologies are well developed. If iso-octane is used instead of MTBE, it has a very low solubility in water, and it is readily biodegraded along with other components of conventional gasoline. It is likely that natural attenuation will be applicable at the same rates as for conventional gasoline. Above-ground treatment costs may increase at most 10% relative to treating water contaminated by conventional gasoline that translate to an annualized cost increase of $600,000 to $10 million.

Direct Costs

Blending MTBE, ethanol or other compounds with gasoline can result in increased costs. Blending MTBE with gasoline at 11% by volume results in an increase of 1 to 5 cents/gallon. The extra cost of using MTBE to meet CaRFG2 requirements, considering an annual consumption of 13.5 billion gallons, is $135 to $675 million. Although small, the price increase is significant.

The California Energy Commission has conducted a study of the supply and cost of gasoline alternatives to MTBE that includes ethanol (10). The estimated unit price increase ranges from 1.9 cents per gallon to 6.7 cents per gallon. Transportation costs and costs of equipment for blending at terminals are included in the calculation of obtaining ethanol from Midwestern U.S. producers and Brazilian producers.

The additional cost of producing a non-oxygenated gasoline is estimated to range from 0.9 to 8.8 cents/gallon or from $141 million to $1.3 billion per year (10).

Another component of the overall direct price is the effect of the blending components on fuel consumption. Gasoline consumption increases when oxygenates are added to conventional gasoline, due to a reduction in the energy content of the gasoline. The opposite occurs for the non-oxygenated gasoline formulations, where the energy content increases by about 0.8 to 1.2% depending on the amount of toluene or alkylate used.

A number of additional costs were identified in our analysis, including the damages to ecosystems, the economic cost of restricting motorboats at multi-use drinking water reservoirs, legal costs, etc. They are discussed in more detail in (11).

Summary of Costs and Benefits

Figure 1 presents the costs and benefits for the three formulations studied, indicating our high and low estimates for the costs and benefits, based on the uncertainties associated with the data. Costs (relative to the baseline, conventional gasoline) are presented in parenthesis. We have stacked up the costs and benefits, to provide a visual appreciation of the size of our cost estimates relative to the benefits. All the formulations represent a net cost (with the low estimate for non-oxygenated gasoline close to zero cost), with MTBE representing the most expensive option.
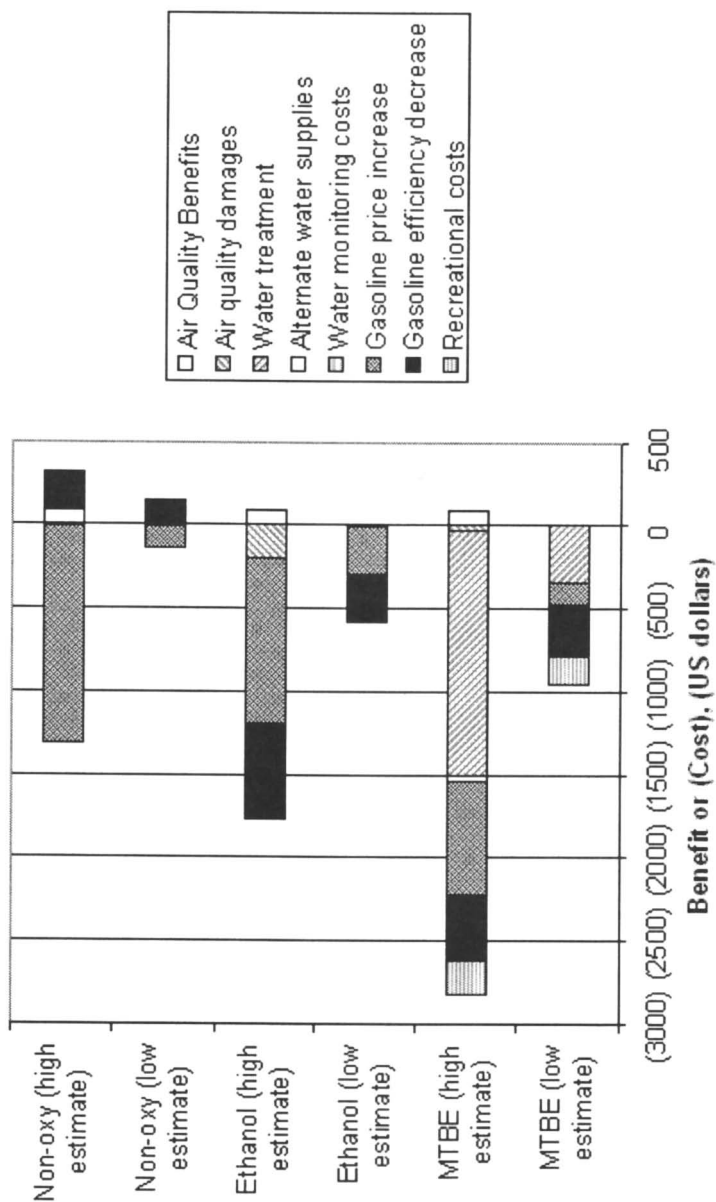
Figure 1. Annualized Cost and Benefit Analysis of Gasoline Formulations in California

Conclusions

In hindsight, it is clear that reformulated gasoline with MTBE was an expensive solution to air quality problems. Spending 1 to 3 billion dollars a year in California alone certainly seems unjustified, once a thorough analysis of the costs and benefits is performed. The major uncertainties were the rate of biodegradation, the toxicity of MTBE and its organoleptic properties. It should have been more evident that a gasoline component used in such large quantities would make its way into the environment and cause more damages than benefits. The existing fate and transport data indicated that there was a possibility that such a gasoline component, used in large quantities would make its way into the environment, with the potential for causing more damages than benefits. The belief that the upgraded USTs would eliminate all spills was perhaps a factor in the decision-making process of oil companies. Granted, a decade ago not all the information needed to make this analysis was available, but the cost of such a research program would have been low, and could have been implemented and completed *before* the large scale introduction of MTBE. Remarkably, even today, there has been no coordinated effort by national or international authorities to reduce the uncertainties associated with MTBE.

We realize that some of the costs for CaRFG-MTBE overlap and therefore, the net costs represent an upper bound. For example, if water treatment costs are incurred to clean up water supply, the costs for alternative water supply will not incurred, except for the immediate supply of water prior to treatment being completed.

Our study considered MTBE replacements to begin the process of evaluating options before another fiasco occurs. It would be unacceptable to find out in a few years from now that we have a new problem with ethanol, toluene or alkylates. We have evaluated the existing information, and in our opinion the non-oxygenated option appears to create less risks than MTBE or ethanol. There are some clear benefits of using ethanol, since it is a renewable resource. The use of ethanol produced from biomass would also reduce carbon dioxide emissions, a major greenhouse gas. However, the potential air quality damages need to be assessed, and the effect on the price of gasoline should be considered relative to other alternatives. We should also begin to consider the source of all this biomass. If we can use current agricultural waste products (e.g. corn stalks, rice straw), then this will be a beneficial shift in the source of our fuel supply. But if it requires significant deforestation around the world to produce enough ethanol for US or worldwide demand, then other options should be explored.

Thus the need to apply the Precautionary Principle to any gasoline blending component, and insist on a thorough evaluation of the implications of such a decision. We must be much more certain of the toxicity, persistence and

bioaccumulation of gasoline blending components, since it is a given that these chemicals will be used in large amounts throughout the world. Let's not make the same mistake again.

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Chapter 10

Stability of Methyl *tert*-Butyl Ether, *tert*-Amyl Methyl Ether, and Ethyl *tert*-Butyl Ether in Acidic Media

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Abstract

MTBE has limited stability in water acidified with either mineral or organic acids and it reacts to produce methanol and butene. This reaction proceeds even in very dilute acid solutions and with weak acids such as acetylsalicylic acid and citric acid. This reaction is not unique to MTBE but is also important with the other structurally similar tertiary alkyl ethers being considered for use as oxygenates in gasoline. The kinetics of these reactions are described in this chapter and are compared to literature results where acid conditions are important to the reactions of MTBE.

Introduction

The release of reformulated gasoline into the environment is a concern because methyl tertiary butyl ether (MTBE) has been detected in ground and surface water sites, and imparts undesirable taste and odor characteristics to the drinking water (*1-5*), plus possible health risks (discussed below*)*. MTBE is quite miscible with water and resistant to biodegradation. This combination of properties makes it very mobile and persistent in the environment (*1,4*). However, this persistence does have a limit, especially in mildly acidic conditions, where it is expected to react chemically. An understanding of this chemical behavior may be

useful for the remediation of water contaminated with fuel oxygenates. This is the topic of this chapter.

This chapter describes the hydrolytic decomposition of three tertiary alkyl ethers (t-alkyl ether 'oxygenates' for reformulated gasoline) in mildly acidic aqueous media, pH 5 at room temperature; namely, MTBE, t-amyl methyl ether (TAME), and ethyl t-butyl ether (ETBE). The literature reports describing the acid catalyzed transformations of MTBE in toluene and gas phase conditions (6,7), suggest that MTBE will have some hydrolytic reactivity in dilute aqueous acid media to produce butene, t-alkyl alcohol and methanol products. Thus, laboratory experiments were designed to determine the hydrolytic reactivity of MTBE in dilute aqueous acid solutions and the effect of the concentration and chemical structure of the acid on the reaction kinetics. The questions before us were, will MTBE and its analogs degrade in water at with a pH slightly less than 7. If so, what is the reaction rate in dilute aqueous solutions containing environmentally compatible acids? Will the results extrapolate to very dilute 'oxygenate' and acid concentrations? Can this reaction be transferred to environment conditions? For background purposes, an introductory review of the structure and hydrolytic chemistry of t-alkyl ethers is included, and our results are compared with other studies where we consider the acid catalyzed reactions to be important.

MTBE Use and Environmental Behavior

Before proceeding with the technical aspects of this chapter we felt it appropriate to review briefly the use and environmental considerations surrounding MTBE. MTBE has been formulated into gasoline in increasing amounts as early as the mid 1970s and more recently in the range of 11 % to 15 % by volume of gasoline following the Clean Air Act amendments of 1990. References to potential use of MTBE in gasoline appear in the literature prior to the 1950s suggesting some earlier usage. MTBE is among the 50 highest produced chemicals in the US and is used almost exclusively in gasoline. It has a high octane rating, low production cost and can be produced at the refineries.

As with all the components in gasoline, the containment of MTBE has been marginal and significant amounts of MTBE have made their way into the environment from leaking underground storage tank systems and pipelines, surface fuel spills, personal watercraft, and atmospheric deposition. MTBE usage has had profound impacts on groundwater nationwide and especially in California within the last decade (8). To date, MTBE has been detected in 40 public drinking water wells, 18 major reservoirs and >10,000 shallow groundwater sites in California (9). Most sites have measured levels below 10 ppb. although there are some notable exceptions such as the City of Santa Monica where the level has been as high as 610 ppb. This is a concern because of the health risks associated with MTBE. Although inhalation studies for MTBE have suggested a low potential for health risks, conclusive data from ingestion studies have yet to be obtained. The US EPA has tentatively classified MTBE as a possible human carcinogen, and has issued a drinking water advisory of 20 to 40 ppm (10). The California Department of Health Services has adopted a secondary MCL (maximum concentration level) of 5 ppb, based on taste and odor and proposed a primary MCL of 13 ppb.

If left unchecked, MTBE will continue to contaminate groundwater supplies, because unlike the other components in gasoline, it is quite miscible with water and travels with the water flow paths. In addition, MTBE can be persistent in the environment because it is resistant to chemical and biological degradation (1,4). Therefore, it is important to both stop the continued release of MTBE into the environment and to remove the MTBE currently present in the groundwater supplies. The latter will be expensive where estimates for the clean-up effort approximate $1.5 billion. $150 million for Santa Monica alone.

There are many technologies to degrade MTBE in contaminated waters. There are physical methods used for removal, not degradation, of MTBE, such as air sparging (11) and adsorption with pack beds of granulated activated carbon, soils and high silica zeolites (12-16). There are irradiation methods based on photocatalysis and high energy irradiation (17); and there are the biochemical methods. Some of these methods are showing technological success and are being commercialized. Then, there are chemical methods which often involve

the use of acid media; for example, the oxidative processes involving Fenton's reagent (*18,19*), peroxy acids (*20,21*) and advanced oxidation processes (*22,23*). Many of these methods are discussed in the other chapters of this book and are not discussed further here. However, acid degradation is also one such chemical process which shows promise and is described in this chapter.

t-Butyl Ethers: A Brief Review

It may help to review the structural characteristics of the t-butyl ethers, of which, MTBE is the smallest member of the class. This review will point to the similarities between the class members and permit some extension of the results found with the lower members to the higher members. The general formula for alkyl ethers is R-O-R', where R and R' are alkyl groups (of any size and may be the same group) and -O- is the oxygen atom bonded in the ether form to the groups.

In the chemical structure of MTBE, one R is a t-butyl group, and the other is a methyl group. MTBE is represented by the chemical structure in Figure 1. The butyl group is designated as tertiary, because the carbon bonded to the oxygen has 3 other carbons bonded to it. Other members of the t-alkyl ether class are, t-amyl methyl ether (TAME) and ethyl t-butyl ether (ETBE) also shown in Figure 1. TAME and ETBE both have one more carbon, or methylene group (underlined) than MTBE, and have a different structural arrangement from each other. Examples of other members of this series (e.g., t-hexyl methyl ether and t-heptyl methyl ether) also can be compared to MTBE in Figure 1 by the underlined methylene groups. For the higher analogs with hexyl (Hx) and heptyl (Hp) groups, several isomers exist and only one is shown.

The t-alkyl ethers have similar physical properties which vary in a regular manner with the structure of the compound. Methyl tertiary butyl ether (MTBE) is a clear liquid at room temperature. It has solvent-like properties and is miscible with water and with most organic compounds. It is volatile, flammable and has a distinct turpentine-like taste and odor, even at the 2-3 ppb level. The larger and heavier members in the series are less volatile, are more oil-like and, correspondingly, less miscible

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with water. The physical properties of the various oxygenates can be compared in Appendix A.

$$
\begin{array}{ccc}
CH_3 & CH_3 & CH_3 \\
CH_3\ C\ O\ CH_3 & CH_3\ \underline{CH_2}\ C\ O\ CH_3 & CH_3\ C\ O\ \underline{CH_2}\ CH_3 \\
CH_3 & CH_3 & CH_3
\end{array}
$$

Methyl-t-butyl ether   t-Amylmethyl ether   Ethyl-t-butyl ether
MTBE   TAME   ETBE
$(C_4H_9OCH_3)$ $(C_5H_{11}OCH_3)$ $(C_4H_9OC_2H_5)$

$$
\begin{array}{cc}
CH_3 & CH_3 \\
CH_3\ \underline{CH_2\ CH_2}\ C\ O\ CH_3 & CH_3\ \underline{CH_2\ CH_2\ CH_2}\ C\ O\ CH_3 \\
CH_3 & CH_3
\end{array}
$$

t-Hexylmethyl ether   t-Heptylmethyl ether
THxME   THpME
$(C_6H_{13}OCH_3)$ $(C_7H_{15}OCH_3)$
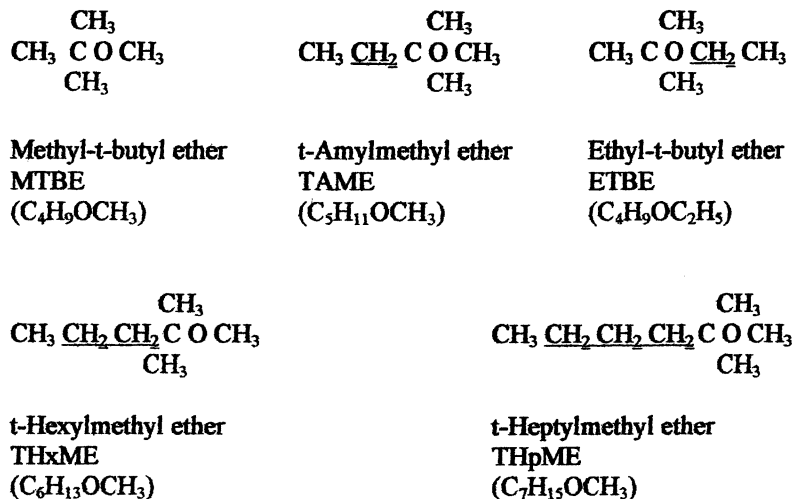
Figure 1. Chemical structures of some tertiary alkyl ethers.

The chemical properties, on the other hand, are much more similar. In general, alkyl ethers are known to be remarkably stable, where harsh chemical conditions must be applied to make them react (transform, degrade, etc.). However, the presence of the t-alkyl group in the structure of the ether makes these compounds chemically more reactive than the rest of the alkyl ethers. The t-alkyl ethers will undergo a hydrolytic reaction which is promoted by acid and higher temperatures (*24*). This is shown schematically in Equation 1 for MTBE. Thus, strong acid and high temperature conditions are often employed in the laboratory experiments to bring about the reaction in a reasonable time interval. The products of the reaction are often a mixture of the alcohol from each R group and the olefin from the t-alkyl group. The relative amounts of these products depends on the reaction conditions. In the case of MTBE, the products are some combination of t-butyl alcohol, methanol and butene. Water is stiochiometrically involved in the reaction to the extent (f) that t-butyl alcohol is produced and remains stable under

the conditions of the reaction (See Equation 1). Based on known chemistry, similar reactivities are expected for the various t-alkyl ethers, under similar reaction conditions. The questions are, how reactive are these t-alkyl ethers in mild acid and ambient conditions? Are the rates of reaction sufficiently fast and the conditions reasonable for this to be a practical approach to the removal of these oxygenates from the environment?

$$\text{t-BuOMe} + \text{(f) } H_2O \longrightarrow \text{(f) t-BuOH} + \text{MeOH} + \text{(1-f) Butene} \qquad 1$$

Acid Catalyzed Reaction of MTBE, TAME and ETBE in Water

The experiments described in this section were performed to demonstrate the feasibility of the MTBE, TAME and ETBE hydrolytic reaction in dilute aqueous acid conditions. It was observed that in aqueous solutions with pH near 5, containing 20 -100 μM concentrations of ascorbic acid, acetylsalicylic acid or oxalic acid, the MTBE concentration decreased with time. The parallel experiment with no acid in the solution showed no reduction in MTBE concentration within experimental error for a similar time period. In most cases, approximately half of the MTBE disappeared in 120 hours. No t-butyl alcohol (TBA) product was detected suggesting the reaction produces butene which most likely escapes from the solution. This is not surprising since TBA is not stable in these conditions as discussed below. The increase in the methyl alcohol product was observed and accounted for in the relative peak areas on the chart.

The decrease in MTBE with time was fit by a first order rate expression, and the rate constants, k', were determined graphically from plots of log[MTBE] versus time. The k' and the statistical fit values are listed in Table 1. This reaction order is reasonable considering that [acid] and [water] do not enter into the stoichiometry of the reaction and remain constant. This provides the over-all rate expression, rate/[ether] = k', where k' is defined equal to k [water] [acid]. Since k' incorporates the acid concentration, [acid], it is expected to vary with [acid]. This was

found to be the case. The k' values are in the range 4 to 10 x 10^{-5} min^{-1} and have reaction half-lives equal to 150 - 300 hours. This implies 99.9% reduction of the MTBE content in 1500 - 3000 hours, or 60 - 120 days at these conditions. The k' values are listed in Table 1. The variation in the k' between repeat runs was 11-26%. With the ascorbic acid experiments, the k' was the same in both distilled and tap water. To determine the effect of salt on the reaction potassium iodide was added to the solution and found to have a small positive effect on k'. Similar reactivities were observed with TAME and ETBE in the solutions containing dilute concentrations of the organic acid. Finally, TBA was found to react 25 times faster than the t-alkyl ethers. Therefore, TBA does not survive the reaction conditions and f in Equation 1 is zero. Equation 1 can be written more simply as in Equation 2.

$$t\text{-BuOMe} \longrightarrow MeOH + Butene \qquad 2$$

Thus, MTBE, TAME and ETBE do degrade at a reasonable rate in dilute aqueous acid solutions. The reaction proceeds with organic acids of the type that are considered 'environmentally friendly'. The reaction rate was also measured with over the counter aspirin and found to be slower than with reagent grade acetylsalicylic acid. Likewise, the reaction rate was measured with over the counter vitamin C. In this case, the k values were very close to the values with ascorbic acid.

The reaction rates follow first order kinetics. This is important because it implies that the rate constants can be used to calculate the fraction 'oxygenate' reacted (or remaining) for a wide range of oxygenate concentrations. There is no apparent sensitivity to the chemical structure of the acid, probably due to the fact that at these low concentrations molecular acids are ca. 60% dissociated and the anion probably has no role in the reaction. The response to the structure of the t-alkyl ether is surprisingly small, and suggests that this chemical behavior can be expected to be similar for many of the analogous t-alkyl ether oxygenates.

The MTBE in aqueous solutions also decreased with time when in contact with a 1% sulfonated polystyrene resin. These solutions were gently rolled to maintain contact between the two phases at ambient

temperature. This sulfonated polymer was selected because it is insoluble in water and easily recovered, yet provides acidity to the solution. This amount of partially sulfonated polystyrene used was calculated to provide a 0.0076 – 0.019 mM acid solution and have pH 4.5, when all of the sulfonate groups are in contact with the water. The measured pH was 5.

Table 1. Degradation of t-Alkyl Ethers in Aqueous Acid Media

Acid	Conc. μM	$10^5 k'$, min^{-1}	r^2
MTBE (8.39 mM)			
Ascorbic Acid	24.2	8.07	0.9956
Ascorbic Acid	48.4	9.10	0.9982
Ascorbic Acid (tap water)	48.4	9.93	0.9695
Ascorbic Acid/KI	48.4/60.2	8.67	0.9792
Ascorbic Acid/KI	48.4/6020	20.17	0.9195
Oxalic Acid	62.5	5.92	0.9978
Oxalic Acid	125	6.13	0.9917
Acetylsalicylic Acid	55.5	10.00	0.9420
Aspirin	27.8	4.37	0.9400
Aspirin	55.5	6.28	0.9467
Polystyrene, 1% acid	7.60	4.75	0.9750
Polystyrene, 1% acid	19.0	6.51	0.9649
TAME (5.73 mM)			
Ascorbic Acid	48.3	11.8	0.9557
Oxalic Acid	125	13.9	0.9914
Acetylsalicylic Acid	55.5	15	0.9685
ETBE (5.73 mM)			
Ascorbic Acid	48.3	14	0.9579
Oxalic Acid	125	10.2	0.9791
Acetylsalicylic Acid	55.5	8.13	0.9810
TBA (1.06 mM)			
Ascorbic Acid	48.3	347	0.97
Oxalic Acid	125	345	0.92
Acetylsalicylic Acid	55.5	347	0.97

Acid Catalysis in Other Chemical Reactions of MTBE

Having demonstrated that MTBE does undergo acid catalyzed hydrolysis, it is important to ask whether the acid catalyzed hydrolysis of MTBE could be important in some of the oxidative degradation processes being considered for the treatment of contaminated waters. In fact, many of these processes are carried out in acidic media, for example, Fenton's reagent, peroxy acids and electrolysis. Even the irradiation methods generate local acid environments. A brief description of selected chemical approaches are described below.

MTBE was transformed to the ethyl ether in toluene containing ethanol in a reaction catalyzed by p-toluenesulfonic acid (TsOH, 0.09 – 0.37 M). In a report by Kogelbauer, et al., (7), MTBE undergoes this a trans-alkylation reaction in toluene at 65 °C (Equation 3). The experiment was carried out in concentrated solutions, 2.9 M MTBE. The reaction proceeded slowly and reached the equilibrium state of 45% conversion in ca. 25 hours. While the reaction conditions, i.e., high concentrations, high temperature and toluene solvent, are remote from the interest of this chapter, this work is a important because it demonstrated the reactivity of MTBE.

$$t\text{-BuOMe} + \text{EtOH} \longrightarrow t\text{-BuOEt} + \text{MeOH} \qquad 3$$

Neat MTBE rapidly decomposes in tens of seconds to produce butene and methanol when in contact with boron pentasil Zeolite, SiO_2/B_2O_3, (Equation 4). In this report by Mildner, et al., (6), the reaction conditions were atmospheric pressure and temperatures between 80 and 140 °C. In this process the MTBE molecules react on the acid sites of the zeolite.

$$t\text{-BuOMe} \longrightarrow \text{Butene} + \text{MeOH} \qquad 4$$

The oxidation of MTBE (ppm range) in Fenton's solution occurs at temperatures up to the boiling point of water due to the exothermicity of the reaction. In a report by Pucik, Schreier and Maslanka, (19), the complete oxidation of MTBE by the hydroxyl radicals produced by this reagent occurred in 6 - 24 hours in a solution pH 3 containing 1-5%

H_2O_2 and 275 mg/L Fe(II). The products were carbon dioxide and water (Equation 5).

$$t\text{-BuOMe} \longrightarrow CO_2 \text{ and } H_2O \qquad 5$$

These reactions were selected for discussion here because they were performed in acid conditions. To assess the importance of the acid catalyzed reaction in these processes, the reaction times for 50% reaction ($t_{1/2}$) were estimated for each case assuming pseudo first order kinetic behavior, where $t_{1/2} = \ln(2) / k_2 [\text{acid}] = 0.693 / k_2 [\text{acid}]$. These reaction times are listed in Table 2 along with the classification of the reaction. The times can be compared with the $t_{1/2}$ values calculated from our k values (room temperature) adjusted for the [acid]. The times for 50 % hydrolysis at room temperature are ca. 70 minutes at pH 3 and 0.7 minutes at pH 1. Temperature corrections are not possible with the data at hand but it can be seen that the hydrolysis reaction has a competitive rate and must be partially responsible for the decay of MTBE in these conditions.

Table 2. Approximated Hydrolysis Reaction Times

Conditions	Reaction Type	Approx. $t_{1/2}$	Ref.
TsOH/Toluene, 65 °C	Substitution	2 hrs.	7
MTBE/Zeolite, 110–140 °C	Elimination	0.3 min.	6
H_2O_2/Fe(II), r.t. to 100 °C	Oxidation	10 hrs.	19

Volatility of MTBE, TAME and ETBE

MTBE, TAME and ETBE are fairly volatile in ambient conditions and readily escape to the atmosphere. The weight loss due to evaporation from an open container left standing at ambient (18 °C) was linear in time. The rates were in the range 0.1-2 mg/min/cm^2 surface area of neat liquid, and are listed in Table 3. The variation in these values

between repeat measurements was 6-12%. Not surprisingly, the rates scale with the boiling points and the partial pressures of the liquids. The one gasoline sample measured had an overall evaporation rate similar to the rate for MTBE. The evaporation rates for methanol and t-butyl alcohol are provided for comparison.

MTBE also volatilizes out of water at a significant rate when left open to the ambient. The evaporation rate from a 1% MTBE solution with a surface area of 1.13 cm^2 was 8.8 mg/min $^{1/2}$/cm^2, and had a t$^{1/2}$ dependence. This volatilization rate is high even though the Henry's constant of 0.0005 atm-m^3/mol (0.02 unit-less) and the solubility of 5% would indicate otherwise.

Table 3. Evaporation Rates in Ambient Conditions

Compound Neat	_MW_	_BP,_ °C	_P(25°C),_ mm Hg	_Evap. Rate_ mg/min cm^2
MTBE	88.2	55.2	245	2.44
ETBE	102.2	67	152	0.604
TAME	102.2	86	68	0.120
Methanol	32	65	120	1.33
t-Butanol	74.1	82.4	42	0.350
t-Amyl Alcohol	86.1	102	16.5	0.0451
Gasoline, Citgo	(94)*			2.65
Water	18	100	24	0.018

*Approximated MW for gasoline.

In a related experiment, the rate of transfer of MTBE was measured from an open pool of the neat liquid to an open pool of water was measured. These measurements were made in a closed chamber at room temperature. For this experiment, the pool of oxygenate and water were placed 10 cm apart in a closed tubular chamber with a 2.5 cm diameter. Aliquots from the water pool were analyzed periodically and found to have an increasing amount of the MTBE. The MTBE content in the 1 ml water pool increased linearly with time during 19 hours at which time the concentration was 0.035g MTBE/g water. For comparison, the reported solubility of MTBE is 0.048g MTBE/g water. A transfer rate coefficient equal to 0.027 mg/min cm^2 was calculated using the 1.13 cm^2

surface area. Parallel results were found with TAME, where a concentration of 0.0038g TAME/g water was found at 9.5 hours. The reported solubility for TAME is 0.020g TAME/g water, and the transfer rate coefficient calculated from the results was 0.0059 mg/min cm^2 Thus, MTBE is ca. 20 times more volatile than TAME and transfers from an open pool of the neat liquid to a pool of water ca. 8 times faster.

Experimental

Reagent grade MTBE, Aldrich Chemical Co., was used in these studies. Commercially available oxalic acid, acetylsalicylic acid and ascorbic acid, reagent grade, were used. The aspirin was a generic brand. The partially sulfonated polystyrene (1% sulfonation) was available from previous studies. Methanol was used as an internal standard for the measurement of the MTBE content. Quantitative determinations were made on a Hewlett Packard 5890A chromatograph and using a 30 m RTX5 capillary column. The column conditions were 40 °C and 16 psi.

The acid catalyzed degradation of MTBE was measured in aqueous solutions containing 0.74 mg/ml MTBE (8.39 mM) and 0.1% methanol (35 mM, internal standard) and the appropriate amount of organic acid. The solutions were kept at room temperature in sealed 4 ml sample vials, and aliquots of the solution were periodically removed for analysis over a 23 hour period. The MTBE/MeOH ratios from the gas chromatograph traces were calibrated to weight ratios and adjusted for the production of methanol during the reaction. The adjustment was small where at 50% reaction the correction applied to the ratio was ca. 11%. The same procedure was used for the other t-alkyl ethers.

Two milliliters of the solution were combined with 0.2 g of a partially sulfonated polystyrene in a 4 ml sample vial and sealed. This amount of sulfonated polystyrene corresponds to a 0.05 mM solution. The mixture was kept at room temperature and gently rolled to provide mild agitation to maintain contact between the two phases. The evaporation rates were carried out gravimetrically using 4 ml glass sample vials left open to the ambient. The surface area of the liquids was 1.13 cm^2.

Conclusions

The persistence of MTBE in ground and surface water results from its high mobility in soil and water and stability to degradation both bio-chemically and chemically. However, we have shown that with a small adjustment of the pH to mild acid conditions. These ethers hydrolyze to produce butene and methanol at reaction rates practical for environmental situations. Since the reactions follow pseudo first order kinetics, the reaction half-lives apply equally well to the very dilute MTBE concentrations. Under the conditions of this study, the reaction half-life was approximately 5 days, which indicates that MTBE *could* degrade 99.9% in approximately 50 days. We have also shown that the pH can be adjusted with common organic acids and that the reaction is not unique to MTBE. TAME and ETBE show the same reactivity. The degradation rate of these oxygenates in mildly acidic water is much faster than the *in-situ* biodegradation rates found in model column aquifers, which have an average reaction half-life equal to approximately 2 years (*16,17*). In mildly acidic water, t-butyl alcohol is found to be even less stable than the oxygenates. Therefore, it does not accumulate as found in the model column aquifers.

Higher members of this t-butyl ether series increase in size by (CH_2) units, in increments of 14 MW units. Accompanying this increase is a change in the physical properties, such as a decrease in volatility and miscibility with water, and a decrease in the oxygen content in the composition, but not necessarily a change in the chemical properties. Therefore, compared to MTBE, the use of other t-butyl ether oxygenates in gasoline would result in a different behavior in the environment. The other oxygenates are predicted to be less mobile. The reduced miscibility with water implies greater adsorption by the soil and plume reduction both in size and concentration. This loss in mobility provides time to complete the hydrolysis reaction. However, the other oxygenates provide less oxygen and would required greater amounts to maintain the same oxygen level in the fuel, i.e., they would be less cost effective.

y Bioquimica, Durango, Mexico, and Sean Tobin, a student at SJSU, for their technical contributions, and Dr. Melanie McNeil provide access to her laboratory facilities.

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*These results were presented in preliminary form in the Symposium on "Exploring the Environmental Issues of Mobile, Recalcitrant Compounds in Gasoline", 219th American Chemical Society Meeting, SF CA, March, 2000.

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Chapter 11

The Electron-Beam Process for the Destruction of Methyl *tert*-Butyl Ether

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Large-scale studies were conducted to examine the effectiveness of the electron beam process to treat water containing MTBE. The source of the water for the experiments was treated ground water (Miami, FL drinking water) to which varying concentrations of MTBE were added. Experiments conducted at low concentrations (~500 µg L^{-1}) and at high concentrations (~2,000 and 31,000 µg L^{-1}) demonstrated that the process can achieve destruction of the MTBE over a wide concentration range. Preliminary kinetic modeling shows good agreement at a lower pH, while the difference between the observed and modeled results at higher pH are most likely attributable to the presence of monochloramine in the water used to conduct the large-scale studies.

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High-octane oxygenated additives useage have increased in the US since their introduction in 1975 (*1*). Methyl *tert*-butyl ether (MTBE) is the most commonly used gasoline oxygenate (*2, 3*) and the compound for which there exists the greatest literature database. The initial environmental concern for MTBE was its occurrence in the air via vehicle exhausts (*3*). However, there has been a growing concern over its occurrence in ground water. MTBE has two major sources in ground water, 1) leaking underground gasoline storage tanks (*4*), and, 2) transport from the gas phase (*5*). MTBE is extremely soluble in water, with a maximum solubility of 48,000 mg L^{-1} (*4*) and is not readily biodegraded (*6*). Its presence in groundwater poses a potential health problem (*7, 8*). Another problem that may be a "driving force" for control of MTBE in drinking water is the organoleptic sensitivity of MTBE. According to Pontius (*9*), humans can smell MTBE at concentrations between 13.5 and 45.4 μg L^{-1}; however, the lowest concentration known to have an adverse health effect on any organism is 145 μg L^{-1}.

Buckley *et al.* (*10*) have shown that MTBE can accumulate in the blood stream and can also be detected in breath. The documented effects of MTBE exposure are headaches, vomiting, diarrhea, fever, cough, muscle aches, sleepiness, disorientation, dizziness, and skin and eye irritation (*8*). MTBE is a suspected carcinogen; however, considerable additional work is necessary to better define its health effects (*8*). The EPA suggested limit is 20 - 40 μg L^{-1} in drinking water (*2, 9*).

Various treatment technologies have been tested for removing MTBE from ground water. The addition of hydrogen peroxide showed very limited success (*11*). However, if Fe(II) was also added (Fenton's reagent), the amount of MTBE degradation increased significantly (*11-13*). The reaction by-products identified were acetone and *tert*-butyl alcohol (TBA). TiO_2 slurries in a photocatalytic reactor were able to remove MTBE from water (*14*). A mechanism for the decomposition of MTBE under aerobic conditions using TiO_2 was proposed, and, under these conditions, the rate constant for the removal of MTBE was 1.2 x 10^{-3} s^{-1}.

O_3 or O_3/H_2O_2 successfully degraded MTBE in water. The O_3/H_2O_2 treatment was more effective than O_3, at pH 8 for 80% removal, requiring 3.1 and 5.5 moles of O_3 per mole of MTBE, respectively (*15*). This method was not considered cost effective or technically practical for small-scale systems (*4*). The UV/H_2O_2 process was relatively successful in reducing MTBE concentrations to about 50 μg L^{-1} in 40 minutes from an initial concentration of about 100 μg L^{-1}. This method encounters problems in hard water because of deposits that form on the UV lamp (*4*). However, commercial systems overcome this problem by employing a patented light sweeper system (Calgon Oxidation Systems).

A relatively new and innovative water treatment, the electron beam process, is a method by which both oxidizing and reducing radicals are generated. This process is potentially a cost effective method for destroying

fuel oxygenates and their reaction by-products in contaminated groundwater. In a recent publication (16) the electron beam process was compared to the UV/H$_2$O$_2$ and UV/TiO$_2$ and was shown to be the most energy efficient process for destroying the two com-pounds studied, methylene blue and phenol (these compounds were chosen because comparable data existed).

The underlying chemistry of the electron beam process is radiation chemistry. Irradiation of water using high energy electrons can be described by the following equation (17) where the numbers denote the yield (G-value) of each species per 100 eV absorbed energy.

$$H_2O \ -\Lambda\text{->} \ (2.7) \ \bullet OH, (0.6) \ H\bullet, (2.6) \ e^-_{aq}, (0.45) \ H_2, (0.7) \ H_2O_2, (2.6) \ H_3O^+ \quad (1)$$

The chemistry that is of principal importance with respect to the electron beam process is that of the three reactive species, the reducing species, e$^-_{aq}$ and H$\bullet$, and the oxidizing radical, $\bullet$OH. Table 1 provides an estimate of the concentration of the reactive species at several doses commonly used in the electron beam process.

Table 1. Estimated Concentration of Reactive Species in Pure Water at Several Doses Using High Energy Electron Irradiation.

Dose (krads)	Concentration (mM)			
	e$^-_{aq}$	H$\bullet$	$\bullet$OH	H$_2$O$_2$
100	0.27	0.06	0.28	0.07
500	1.4	0.3	1.4	0.4
1,000	2.7	0.6	2.8	0.7

There have been only limited data reported on the radiation chemistry of MTBE. Eibenberger et al. (18) investigated the radical intermediates formed upon $\bullet$OH attack on MTBE in the presence of tetranitromethane (TNM). TNM was used to probe carbon-centered radicals (19-28) by the formation of the relatively stable nitroform anion (NF$^-$) which strongly absorbs at 350 nm (ε_{350nm}= 15,000 M^{-1} cm^{-1})(19). From their findings they suggested the formation of two different MTBE radical intermediates that subsequently react with TNM, reactions 2 – 4.

$$(CH_3)_3COCH_3 + \bullet OH \ \longrightarrow \ (CH_3)_3CO \ H_2C\bullet \quad (2)$$
$$-H_2O \qquad A$$

$$(CH_3)_3COCH_3 + \bullet OH \ \longrightarrow \ \bullet CH_2(CH_3)_2COCH_3 \quad (3)$$
$$-H_2O \qquad B$$

$$A/B + TNM \longrightarrow NF^- + products \quad (4)$$

The branching ratio of reactions 2 and 3 was shown to be 71:29 with the overall bimolecular reaction rate constant for hydrogen abstraction by •OH as 1.6×10^9 M^{-1} s^{-1}. This latter value suggests that the electron beam process (given the relatively high concentration of •OH, Table 1) would be an efficient process for the destruction of MTBE in water (18).

This paper reports the results for the large scale removal of MTBE at the Miami, FL, electron beam facility. The studies were conducted at 100 gallons per minute (gpm), at low and high concentrations, and serve as a basis for preliminary estimates of treatment costs. A kinetic model was also used to predict the removal of MTBE from the treated groundwater and to provide information for guiding future research in the destruction of MTBE in aqueous solutions using the electron beam process.

Experimental Procedures

Materials

MTBE (Aldrich, 99.8%, anhydrous) was obtained at the highest purity available and used as received for large-scale experiments.

Methods

MTBE Analysis. Static and dynamic headspace sample concentrations methods were used with a gas chromatographic determination (Model 5890, Hewlett Packard) for the determination of MTBE concentrations.

MAKSIMA-CHEMIST Kinetic Model. The computer code called MAKSIMA-CHEMIST provided by the Atomic Energy of Canada (29) was used as the starting point for the kinetic model. This program uses a method based on the Gear predictor algorithm for integration. Further details of the integration algorithm and validation tests can be found elsewhere (29, 30). MAKSIMA-CHEMIST has satisfactorily predicted results for irradiation of water (31). The input to the kinetic model includes a list of all reacting species, their initial concentrations, as obtained from the experimental measurements, and the corresponding rate constants. The water residence time in the irradiating region was estimated at 0.091 second. In addition to the organic solutes, there are other solutes, such as O_2, and reaction by-products that compete for the reactive species. The predictability of the model depends greatly upon the ability to account for all the existing reactions with proper rate constants and on the accuracy of the measured dissolved ion concentrations.

Electron Beam Research Facility. All of the large scale studies were conducted at the Miami, Electron Beam Research Facility (EBRF). The EBRF has been described in detail elsewhere (32). Briefly it is a 1.5 MeV, 50 mA, horizontally scanned beam capable of treating up to 150 gallons per minute

(gpm). Typically experiments were conducted at either 100 or 120 gpm (~0.4 - 0.5 m³/min). The dose, 25 - 800 krads (0.25 - 8 kGy), is continuously variable by varying the beam current. Each experiment consisted of treating a minimum of 3,000 gallons (11.4 m³). A stainless steel tanker was used to prepare the solutions and mixing was accomplished using a 200 gpm (0.76 m³/min) pump to circulate the solution prior to treatment.

Results and Discussion

Four preliminary large-scale experiments were conducted at the EBRF at a flow rate of 100 gpm. Two relatively low concentrations, ~500 to 600 µg L⁻¹ (MTBE detection limit 5 µg L⁻¹) and two relatively high concentrations, 22,000 and 31,000 µg L⁻¹ (MTBE detection limit 87 µg L⁻¹) experiments have been completed.

The lower concentration experiments were conducted using a one-pass experimental set-up (data summarized in Table 2). MTBE determinations were conducted for all samples collected at all doses. The variability in the influent samples resulted from inadequate stirring of the large tank in which the solutions were prepared (17,000 L). (Later experiments were stirred longer prior to running the system to avoid this problem.) The kinetic model was run at each dose using the influent (before treatment) concentration that was determined experimentally.

Table 2. MTBE Destruction using the Electron Beam Process for the Two Low Concentration Samples.

Dose (krads)	MTBE Concentration (µg L⁻¹)		
	Influent	Effluent	Kinetic Model
	pH $\cong$ 9		
50	365	115	96
100	426	32.7	57
300	436	BMDL[1]	1.9
500	488	ND	ND[2]
	pH $\cong$ 6		
50	38	5.7	8.7
100	146	BMDL	6.5
300	472	ND	ND

[1] BMDL = Below method detection limit which was 5 µg L⁻¹
[2] ND = Not detected for analytical results that is below 1 µg L⁻¹, for the kinetic modeling < 0.01 µg L⁻¹

The source water was naturally aerated treated groundwater (Miami, FL potable water). A pH $\cong$ 9 is normal for the treated water. Therefore, we generally conduct experiments at a pH of around 9 and then, by adding acid (HCl), we removed alkalinity and ran addition experiments at pH $\cong$ 6. If a compound is primarily removed via •OH mediated reactions, the presence of the carbonate ion at a pH of 9 adversely affects the removal efficiency. Although this effect was difficult to quantify because of influent MTBE concentrations variability, it did appear that the removal was inhibited at pH 9 when comparing the two experiments.

The high concentration experiments were conducted in a re-cycle mode where the delivered dose was constant and samples, taken with time, reflected an increasing dose. The results, summarized in Table 3, show some scatter as a result of experimental variability encountered in conducting large-scale studies; however, as long as samples are taken for each dose before and after treatment the data can be used to determine dose *versus* destruction. The zero dose samples were taken before the electron beam current was turned on, but while the water was flowing at 100 gpm.

The development of a kinetic model to describe the removal of organic compounds by the electron beam process is one of the long-term goals of our

Table 3. MTBE Destruction using the Electron Beam Process for the Two High Concentration Samples, pH $\cong$ 9.

Dose (krads)	MTBE Concentration (μg L^{-1})	
	Influent	Effluent
Experiment 1		
0	2,290	2,170
100	2,550	484
234	1,640	276
331	773	314
498	423	113
665	88	BMDL[1]
Experiment 2		
0	31,000	37,800
400	24,700	8,390
800	8,860	3,090
1200	3,340	1,430
1600	876	738
2000	BMDL	BMDL
2400	BMDL	BMDL
2800	BMDL	BMDL

[1] BMDL = below method detection limit which was 87 μg L^{-1}

research. The model will assist in better understanding the electron beam process and ultimately in process applications.

Modeling natural waters involves the incorporation of other radical scavengers and pH buffering systems such as the carbonate system in addition to the organic solute(s) of interest. These chemicals, known as scavengers, reduce the overall radical reactivity within the system. The dissolved organic carbon (DOC) also acts as a scavenger. In the case of DOC, rate constants for the reaction of DOC with e^-_{aq} or H• could not be found. An estimated value of the rate constant of OH· with DOC was obtained from (33) of $(6.6 \pm 5.4) \times 10^8$ L mg^{-1} s^{-1}. The inaccuracy of this value poses a problem in simulating destruction results because both the DOC concentration and the rate constant are relatively high compared to other scavengers in the system (34, 35).

The mechanism used in our initial kinetic model for the destruction of MTBE in groundwater is shown in Table 4 (equations 61 - 80). The first 58 equations of the kinetic model, which describe the radiation chemistry of pure water and those reactions that are necessary to account for the presence of alkalinity, dissolved organic matter (DOM), and the nitrate ion, were the same as those used for CCl_4 (36). Reaction by-products are known to significantly affect ability of the kinetic model to predict removal. Therefore, because a detailed mechanism was not known for MTBE, the kinetic model was not used for the high concentration MTBE samples (Table 3). The rate constants for the initial radical reaction with MTBE have recently been evaluated and were used in this simulation (37). The reaction for the carbon centered radicals (equations 2 and 3) with molecular oxygen were also evaluated (37). (In the model, Table 4, PDTS is unidentified reaction products, F is formaldehyde and FA is formic acid.)

Two additional experiments were conducted at a nominal influent concentration of 500 µg L^{-1} MTBE. These data were also modeled and the results are shown in Figures 1 and 2.

The model results as pH = 5.30 agreed closely with those that were determined experimentally. The slight over prediction of the 0.100 Mrad dose presumably resulted from reaction by-products not included in the destruction mechanism. Reaction by-products that are not specified in the model act as radical scavengers and thus compete with the MTBE for •OH.

The results of the model at pH = 8.41 significantly over predicted MTBE removal at all doses. This result (especially at a dose of 0.05 Mrad) suggests that scavengers other than MTBE destruction by-products were present. The first reactant that was not accounted for is the disinfectant NH_2Cl. (NH_2Cl rapidly decomposes at a pH of 5.30 and therefore would not be a scavenger in the experiments conducted at the lower pH.) There were no reaction rate constants for NH_2Cl in the literature and therefore for this modeling approximations were used. Recent preliminary studies suggest that

Table 4. Kinetic Model (Simplified Mechanism) for the Destruction of MTBE in Aqueous Solution.

No.	Reactants		Products	k (M^{-1} s^{-1})
(59)	$NH_2Cl + e^-_{aq}$	$\rightarrow$	PDTS	1.000e+08
(60)	$NH_2Cl + \cdot OH$	$\rightarrow$	PDTS	1.000e+08
(61)	$MTBE + \cdot OH$	$\rightarrow$	$MTBE\cdot + H_2O$	2.000e+09
(62)	$MTBE + H\cdot$	$\rightarrow$	$MTBE\cdot + H_2$	1.000e+05
(63)	$MTBE + e^-_{aq}$	$\rightarrow$	$MTBE^-$	1.750e+07
(64)	$MTBE\cdot + O_2$	$\rightarrow$	$MTBO_2\cdot$	1.240e+09
(65)	$MTBO_2\cdot$	$\rightarrow$	$TBA + F$	1.000e+05
(66)	$TBA + \cdot OH$	$\rightarrow$	$TBA\cdot + H_2O$	6.000e+08
(67)	$TBA + H\cdot$	$\rightarrow$	$TBA\cdot + H_2$	1.700e+05
(68)	$TBA + e^-_{aq}$	$\rightarrow$	PDTS	4.000e+05
(69)	$TBA + CO_3^-\cdot$	$\rightarrow$	PDTS	1.600e+02
(70)	$TBA\cdot + O_2$	$\rightarrow$	$TBAO_2\cdot$	1.500e+09
(71)	$TBAO_2\cdot + H_2O$	$\rightarrow$	$TB(OH)_2$	4.500e+10
(72)	$F + \cdot OH$	$\rightarrow$	FA	1.000e+09
(73)	$F + H\cdot$	$\rightarrow$	$\cdot CHO + H_2$	5.000e+06
(74)	$F + e^-_{aq}$	$\rightarrow$	$\cdot CH_2OH + OH^-$	1.000e+07
(75)	$FA + \cdot OH$	$\rightarrow$	CO_2	1.300e+08
(76)	$FA + H\cdot$	$\rightarrow$	$CO_2 + H_2 + H\cdot$	4.400e+05
(77)	$FA + e^-_{aq}$	$\rightarrow$	FA^-	1.400e+08
(78)	$\cdot CH_2OH + O_2$	$\rightarrow$	$HOCH_2OO\cdot$	4.900e+09
(79)	$HOCH_2OO\cdot$	$\rightarrow$	$F + H_3O^+ + O_2^-$	3.000e+00
(80)	$HOCH_2OO\cdot + OH^-$	$\rightarrow$	$^-OCH_2OO\cdot + H_2O$	1.800e+10
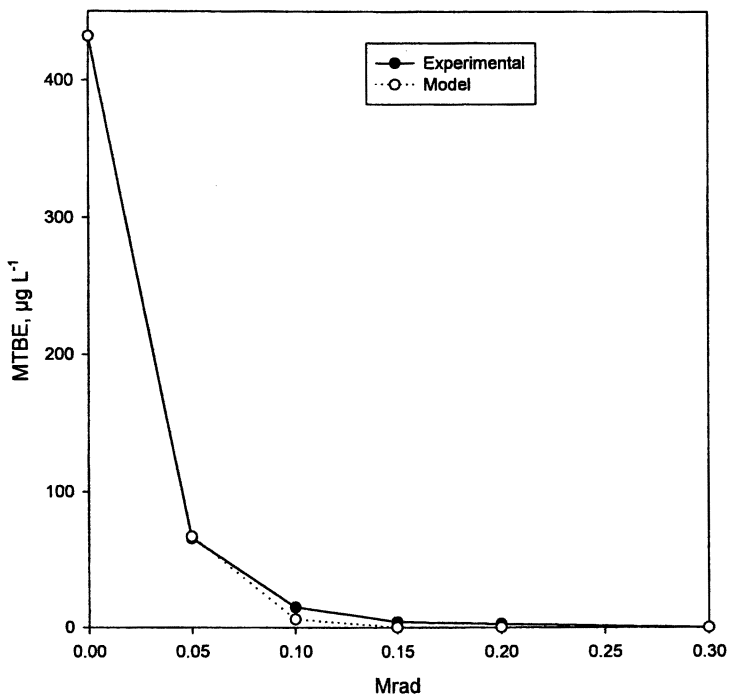
Figure 1. MTBE destruction at a pH = 5.30 using the electron beam process.

our approximations were underestimated by as much as an order of magnitude (*38*). However, a detailed analysis of the data has not been completed and the estimates (Table 4) were used for this simulation.

One of the advantages of the electron beam process over other advanced oxidation technologies is that it forms the reducing species e^-_{aq} and H• at the same time as the oxidizing radical •OH. In studies using ozone based chemistry in natural waters that contain bromide ion, bromate ion, BrO_3^-, is formed. Initial studies in water from the wells in Santa Monica resulted in unacceptably high BrO_3^- formation and the use of ozone has been questioned, at the present time. The electron beam process does not form BrO_3^-. Studies have also shown that, if present, the process can reduce it to Br^- (*39,40*).
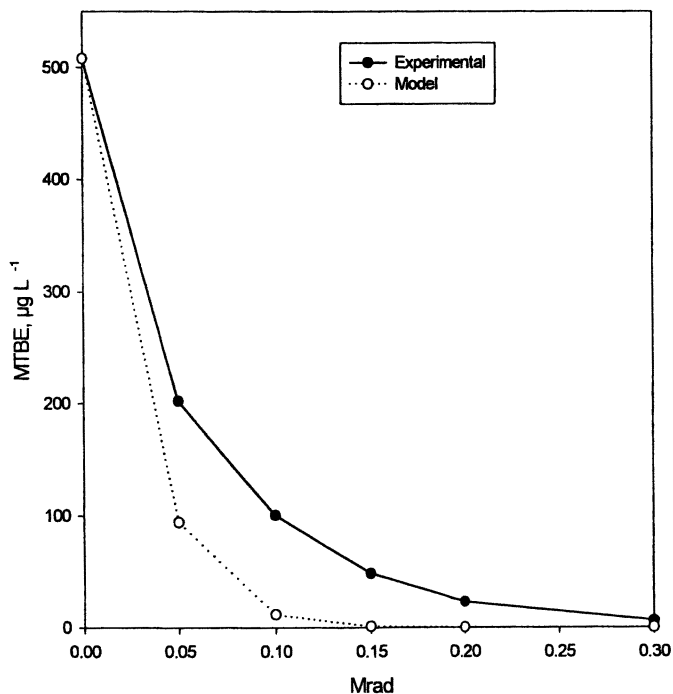
Figure 2. MTBE destruction at a pH = 8.41 using the electron beam process.

Economic Analysis

We have completed a preliminary analysis of the economics of the electron beam process for the removal of MTBE in groundwater. This analysis included a simple depreciation (cost recovery of the capital in five years) and operation and maintenance costs. The specific site that was considered was Santa Monica, CA. It appears that the electron beam process, even without optimization of the process, could treat the water for ~$1.30 per 1000 gallons. Depending on the dose required to completely destroy the reaction by-products that are predicted from the model, the cost may range to $1.50 per 1000 gallons. These costs, although high for a non-contaminated aquifer, are not out of the range being considered. Therefore, we feel that additional, in depth, studies are warranted for the electron beam process.

Conclusions and Future Studies

We have shown that MTBE can be effectively removed from solutions of widely varying concentrations. The details of the complete mechanism for the destruction of MTBE in water using the electron beam process are now just becoming available. To further evaluate this process andother advanced oxidation technologies for the complete destruction of MTBE (and other co-contaminants) a mechanism will be essential. Therefore we feel that there are several investigations that are needed.

1. Additional studies are needed to complete a mechanism for the complete destruction of MTBE. This mechanism must also account for the formation and destruction of reaction by-products.
2. In those cases where co-contaminants are present, their presence will have to be considered as they may impact the removal of MTBE.
3. It is likely that for many of the reaction by-products the free radical chemistry has not been studied and there will be a need for bimolecular rate constants for some of these compounds. These studies will be of interest in the application of all of the advanced oxidation processes, as many of then will share a common destruction mechanism.

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Chapter 12

TiO$_2$ Photocatalysis of Gasoline Oxygenates, Kinetic Parameters, and Effects of Catalyst Types and Loading on the Degradation of Methyl *tert*-Butyl Ether

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The fuel oxygenates, *tert*-butyl methyl ether (MTBE), diisopropyl ether (DIPE), *tert*-amyl methyl ether (TAME), and *tert*-butyl ethyl ether (ETBE) are readily degraded by TiO$_2$ photocatalyst. Complete removal of these substrates can be easily achieved at concentrations up to at least 100 ppm. The observed rate of degradation for MTBE decreases with increasing concentration and while the degradation at a given concentration is consistent with first order kinetics, changes in the kinetic parameters as a function of concentration suggest the reaction is more complex than a simple first order process. A Langmuirian relationship between the initial rate of degradation and initial concentration of MTBE was observed which can be used to predict degradation rates over a wide range of concentrations. The photocatalytic activities of several TiO$_2$ catalysts were measured and the effect of catalyst loading on the degradation rate was studied to determine the optimal conditions for the removal of MTBE.

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Introduction

Alkyl ethers have been introduced into the groundwater in large quantities through leaking fuel tanks and petroleum pipelines and pose a serious environmental problem. These ethers, particularly methyl *tert*-butyl ether (MTBE) were chosen as gasoline additives to produce cleaner burning fuel in response to the federal government's demands for better air quality. But the once-championed MTBE now finds itself at the center of controversy over its potential to contaminate groundwater and its possible health risks (*1*). MTBE contamination has reached such high levels in Santa Monica, California that the city has to import water from other areas. The aroma of MTBE can be detected by humans in quantities lower than the levels being considered unacceptable for health reasons, down to levels as low as 15 ppb, thus creating additional public concern (*2*). The federal government is currently under pressure to ban the sale of MTBE-containing fuel nationwide.

In general, the use of alkyl ethers as fuel additives is a serious problem because they are relatively soluble in water, travel through soil quickly and persist in the environment for long periods of time. Since these ethers do not appreciably absorb light in the near UV/visible region, direct photo-degradation by solar irradiation is very ineffective. In addition, oxidation in aqueous environments with naturally occurring hydroxyl radicals, and other oxidative processes, are too slow to yield significant decontamination. The unreactive nature of these compounds makes them especially persistent in the environment. The effective removal of these substrates by bioremediation (*3,4*), adsorption and air stripping techniques requires special considerations.

Advanced oxidation processes (AOPs) offer a viable treatment option for waters contaminated with MTBE (*5-9*). AOPs generally involve the generation of hydroxyl radicals, which react (through oxidative processes) with a variety of substrates and can lead to complete mineralization of organic substrates. Over the past decade, we have directed our efforts towards a basic understanding of AOPs, specifically TiO_2 photocatalysis, sonolysis and radiolysis (*10-18*). Our initial studies have demonstrated that MTBE is readily degraded upon treatment by these advanced oxidation processes, but the focus of this paper involves TiO_2 photocatalysis of fuel oxygenates.

TiO_2 photocatalysis is initiated when the semiconductor absorbs a photon of appropriate energy generating a conduction band electron (e^-_{cb}) and a valence band hole (h^+_{vb}), eq 1. While transformation (degradation) of the substrate (pollutant) can occur by direct electron transfer to or from the photoexcited TiO_2 in oxygen or air saturated aqueous solutions, the preliminary processes are reduction of oxygen to superoxide anion radical, eq 2, and oxidation of water (or hydroxide) to hydroxyl radical, eq 3. The "hydroxyl radical" is the species that predominantly initiates the oxidation processes leading to mineralization of pollutants by TiO_2 photocatalysis, eq 4.

$$TiO_2 \text{----} hv \text{---} > h^+_{vb} + e^-_{cb} \qquad [1]$$
$$e^-_{cb} + O_2 \text{-------} > O_2^{-\cdot} \qquad [2]$$
$$h^+_{vb} + H_2O \text{-------} > \text{"HO}\cdot\text{"} + H^+ \qquad [3]$$
$$\text{Pollutant (R)} \text{------"HO}\cdot\text{"} \text{-----} > \text{-----} > \text{Mineralization} \qquad [4]$$
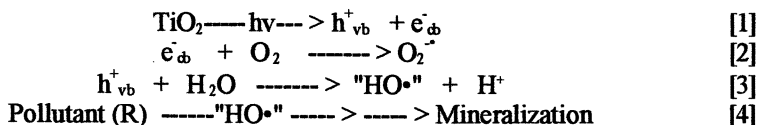
The hydroxyl radicals, "HO•", formed at the surface have been referred to as trapped holes, and likely remain associated with the surface until further reactions occur (*19*). For the purposes of this paper we will simply refer to these reactive species as "hydroxyl radicals".

In this study we found that MTBE, DIPE, TAME, and ETBE are readily degraded by TiO_2 photocatalysis. We have also determined a number of kinetic parameters for the photocatalysis of MTBE. A change in kinetic parameters with increasing MTBE concentration indicates a reduction in reaction order from first to zero order with increasing substrate concentration. The Langmuir–Hinshelwood kinetic model was applied and a correlation between degradation rates and initial concentrations is observed. A photoactivities of different TiO_2 photocatalysts were measured and optimal catalyst loading established for the degradation of MTBE.

Results and Discussion

TiO₂ Photocatalysis of Fuel Oxygenates and Product Studies of MTBE.

We have demonstrated MTBE, DIPE, TAME, and ETBE are readily degraded under conditions of TiO_2 photocatalysis, as illustrated in Figure 1. In a representative experiment, the semiconductor powder was suspended in an air saturated aqueous solution of the ether. Sonication was used to achieve effective dispersion of the semiconductor particles. The suspensions were irradiated in sealed reaction vessels and samples taken at specific time intervals. In the absence of oxygen, light, or catalyst no appreciable degradation of the substrates is observed thus establishing the degradation reactions are in fact a result of photocatalysis.

While the degradation for all the substrates is complete within 60 min, the rate of degradation for DIPE is notably faster than the other substrates. The degradation of these substrates is likely the result of hydrogen atom abstraction by the hydroxyl radical generated during photocatalysis. Hydrogen abstraction of the methine (CH) hydrogen of DIPE leads to a highly stabilized radical and is therefore expected to be faster than hydrogen abstraction of any of the hydrogens on the other oxygenates (*20*). This may be the reason the observed rate of degradation for DIPE is fastest among these substrates.

Although there is limited information available on the photocatalysis of gasoline oxygenates, Barreto, Gray, and Anders identified *t*-butyl formate, *t*-butyl alcohol, acetone, and isobutylene as stable products during the TiO_2

photocatalysis of MTBE (5). In addition, we have identified methyl acetate, formaldehyde, and methane as reaction products from the TiO₂ photocatalysis of MTBE. A reaction profile for the major products of MTBE is illustrated in Figure 2. Under our reaction conditions, TBA is produced in relatively low yields suggesting the rates of formation and disappearance of TBA are comparable. The conversion of TBF to TBA under dark reaction conditions is too slow to account for the observations, indicating this conversion is not the result of simple hydrolysis.

The photocatalysis of TBA yields acetone as the major product. The dehydration of TBA to isobutylene has been proposed (5), but does not occur to an appreciable extent under dark reaction conditions. Although we confirmed that isobutylene is converted to acetone by TiO₂ photocatalysis, isobutylene readily partitions to the gas phase, has low solubility in water, and is not expected to appreciably adsorb onto the TiO₂ surface. Given these characteristics it is unlikely the major reaction pathway leading to the formation of acetone during TiO₂ photocatalysis of TBA involves isobutylene. We propose the major reaction pathway leading to the conversion of TBA to acetone involves the abstraction of a hydrogen atom from the methyl group of TBA (21). Acetone is degraded slowly relative to MTBE but can be eliminated by extended irradiation.

Kinetic Studies

In an attempt to better understand the kinetic parameters for the TiO₂ photocatalysis of fuel oxygenates we chose to study the degradation of MTBE as a function of concentration. The initial concentration of MTBE was varied and the initial degradation measured as a function of irradiation time. First order kinetic models were employed to evaluate the observed rates of TiO₂ photocatalysis. A commonly employed form of the first order rate law is given by eq 5.

$$\ln [MTBE]_0/[MTBE]_t = kt \qquad\qquad [5]$$

A linear relationship between the $\ln [MTBE]_0/[MTBE]_t$ versus time, t, is consistent with first order kinetics in which the slope represents the first order rate constant, k. Plots of $\ln [MTBE]_0/[MTBE]_t = kt$ as a function of irradiation time were constructed, as illustrated in Figure 3, and the pseudo first order rate constants calculated from the slope of the best fit lines.

The rate constants, half-lives and overall rates of degradation are summarized in Table 1. The rates of degradation decrease with increasing substrate concentration and at longer irradiation times. While linearity of the kinetic plots is quite good at a given concentration and hence consistent with a first order process, the change in the rate constant as a function of initial concentration suggests the reaction process is more complex than a simple first
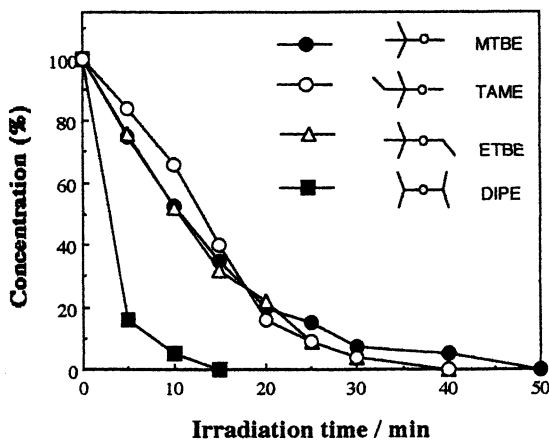
Figure 1. Degradation of MTBE, ETBE, TAME and DIPE by TiO₂* as a function of irradiation time under 350 nm UV light. Initial substrate concentrations were 40-50 ppm.
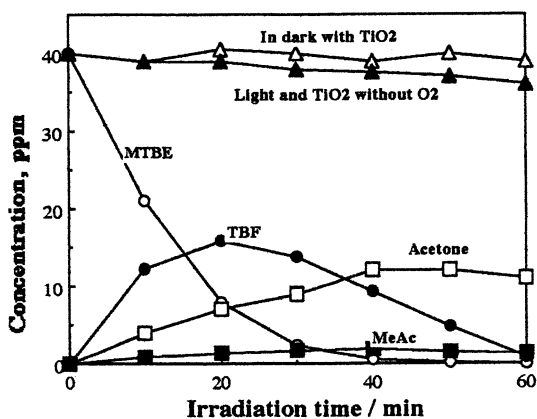
Figure 2. Reaction profile and control experiments for TiO₂ photocatalytic degradation of MTBE.

order reaction. The observed rates increase only fractionally with a five-fold increase in the concentration of the substrate indicating a reduction in the order of the reaction. It has been suggested that such observations are the result of saturation of the catalytic process at high substrate concentrations (*22,23*). At high solute concentrations all the catalytic sites (hydroxyl radical) are occupied and zero order kinetics is observed while at low concentrations the number of active sites is not the limiting factor of degradation which is now proportional to the substrate concentration in accordance with apparent first order process.

Table 1: First Order Kinetic Parameters for TiO₂ photocatalysis of MTBE

[MTBE] (ppm)	Rate Constant, k[a]	R[b]	half-life (min)	rate (ppm/min)
10	0.16	0.997	5	1.6
20	0.09	0.994	8	1.8
35	0.06	0.997	12	2.1
50	0.06	0.996	17	2.0

a - The average of duplicate runs reproducible to within 8-15 %.
b - Correlation coefficient for the best least squares fit line representing the data.

The Langmuir-Hinshelwood (L-H) kinetic model has been extensively used in photocatalysis. The L-H model was initially developed for gas-solid heterogeneous reactions, it has been successfully applied to a variety of photocatalytic systems (*24*). Application of this model assumes that every adsorption site is equivalent and substrate adsorption is independent of whether neighboring sites are occupied or unoccupied. We expect that adsorption < --- > desorption process is an equilibrium between surface adsorbed molecules and those in the solution. The rate of adsorption is proportional to the substrate concentration and the number of active site (or species) such that

$$Rate = k\Theta \qquad [6]$$

Where k represents the proportionality constant and Θ is equal to the surface coverage. The surface coverage is expressed by eq 7.

$$\Theta = K[S]/1+K[S] \qquad [7]$$

Where K is the adsorption equilibrium constant and [S] the substrate concentration. The reciprocal relationship can be obtained from eqs 6 and 7, yielding eq 8.

$$1/\text{rate}_0 = 1/k + 1/kK[S_0] \qquad [8]$$

Where a linear plot of 1/rate vs 1/[S] is consistent with the Langmuir-Hinshelwood model with the slope = 1/k and the intercept =1/kK.

We carried out a kinetic analysis using the L-H kinetic model and employing the degradation rates from the first 10-20 % disappearance of the starting material. At these low conversions the competition between MTBE and the reaction products for the hydroxyl radical is expected to be insignificant. The disappearance of substrate was monitored by gas chromatography and extreme care was taken to ensure uniform experimental conditions. The reciprocal plot of initial rates as a function of initial substrate concentration yields a linear relationship as illustrated in Figure 4. The correlation between the initial rate and initial substrate concentration is consistent with a Langmuirian relationship.

Surprisingly the observed slope of the Langmuir-Hinshelwood plot is negative as opposed to the normally observed positive slope. We attribute this unusual observation to competitive reactions (inhibition) between the starting substrate and the reaction products for surface generated hydroxyl radicals. The experiments were conducted at relatively low conversions to ensure low concentrations of the initial products relative to starting substrate. However the initial products in the case of MTBE are carbonyls and alcohols which will be more strongly adsorbed than the starting ether substrates (25). The reaction products, formed at the surface of the catalyst, are more strongly adsorbed than the starting ether thus subsequent reactions with surface generated hydroxyl radicals are more likely to occur with the products (despite being minor products in terms of the bulk solution) because of higher surface concentration.

The comparison of degradation rates of MTBE mediated by the different types of TiO_2 was performed. It can be seen from Figure 5 that the different types of TiO_2 have important effect on the degradation rates. The degradation of MTBE was insignificant in the presence of the catalysts Hombikat UV 100 TiO_2 and VP F440 TiO_2 doped with 2 % iron oxide relative to degradation by the Degussa P25 catalysts. The faster rates of degradation were achieved with the Degussa P25 catalysts with a surface of 65 m^2/g. Although the presence of dopants can lead to enhanced photocatalytic activity it appears to have a negative effect for the case of the F440 catalyst in our studies. A number of factors may influence the photoactivity of these catalysts (12).

The relationship between the degradation rates and the different loading of the different types of TiO_2 was examined, shown in Figure 6. The optional loading under our experimental conditions is 134 mg and 335 mg / L solution in the cases of P25 (specific surface area 65 m^2/g) and P25 (55 m^2/g), respectively. In the case of Hombikat UV 100 TiO_2, the observed degradation rate increases slightly with the increase in TiO_2 loading in the given range, but still is considerably less photoactive than the Degussa P25 catalysts at much lower loading.
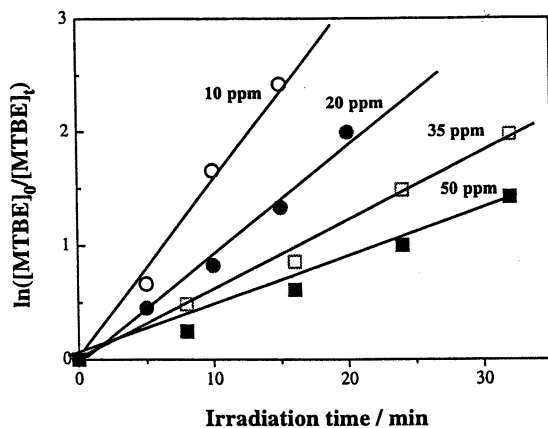
*Figure 3. Plots of ln [MTBE]₀ / [MTBE]ₜ vs irradiation time during
photocatalytic degradation of MTBE.*
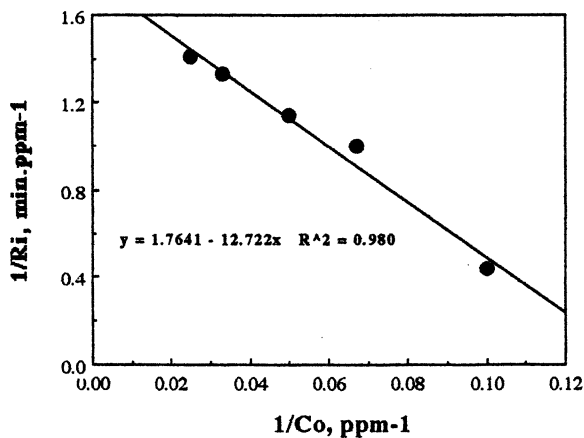
*Figure 4. Langmuir - Hinshelwood plot for the TiO₂ photocatalytic degradation
of MTBE. Initial concentration, 10, 15, 20, 30 and 40 ppm.*
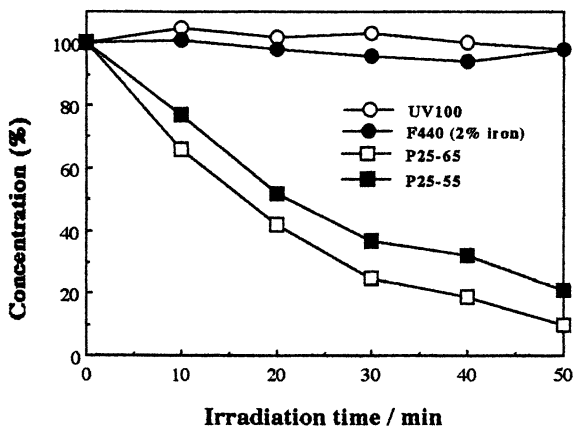
Figure 5. The comparison of MTBE (50 ppm) degradation rates mediated by the different types of TiO₂.
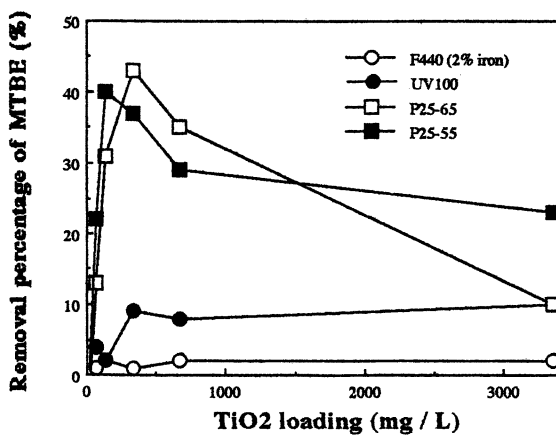
Figure 6. The effect of different loading of a variety of TiO₂ types on the degradation rates. [MTBE], 50 ppm.

Conclusions

The gasoline oxygenates , MTBE, DIPE, TAME, and ETBE are readily degraded by TiO_2 photocatalysis. The kinetic parameters for degradation of MTBE change as the concentration of MTBE increases. At low MTBE concentrations the kinetic parameters are consistent with a first order process whereas at higher concentrations lower order is observed, consistent with saturation of the catalyst. A reciprocal correlation between the initial degradation rates and initial concentrations was also observed. Although the rates of degradation decrease at high substrate concentrations effective degradation of MTBE is easily achieved at the concentrations expected under typical treatment conditions. The Degussa P25 TiO_2 with specific surface area 65 m^2/g exhibits the highest photocatalytic activity. Catalyst loading has a pronounced effect on the degradation rates of MTBE and optimal degradation was observed at a loading of 335 mg / L for the Degussa P25 TiO_2 with specific surface area 65 m^2/g. The results from these studies will be useful in developing predictive models for reactor design and actual water treatment strategies for TiO_2 photocatalysis.

Experimental section

Materials: *tert*-butyl methyl ether, *tert*-butyl formate, *tert*-butyl alcohol, methyl acetate, isobutylene, acetone, n-butanol, butanone, diisopropyl ether, *tert*-amyl methyl ether, and *tert*-butyl ethyl ether were purchased from Fisher or Aldrich and used without further purification. All reaction solutions were prepared using milli-Q purified water. A variety of TiO_2 catalyst, Hombikat UV100 from Sachtleben Chemie (specific surface area ~250 m^2/g), VP F440 TiO_2 2% iron oxide, P25 TiO_2 (specific surface area ~50 m^2/g) and P25 TiO_2 (specific surface area ~65 m^2/g) are used as received (from Degussa).

Equipment: the photocatalytic experiments were carried out in Pyrex reaction vessels equipped with air tight Teflon screw tops. The solutions were prepared using volumetric glassware and the catalyst loading was 100 mg/L unless otherwise specified. The headspace of the reaction vessel was generally purged with air. The sealed reaction vessel was warmed to ~ 44 °C and sonicated using a cleaning bath for 5 minutes to achieve a uniform suspension prior to irradiation. It was established that no appreciable losses of the substrates were observed during the purging, warming or sonolysis procedures. The samples were irradiated at 350 nm using a rayonet reactor which contained 10 bulbs. The intensity of the light specified by the manufacture was recently confirmed using actinometry (*17*). Aliquots (2.5 mL) were taken from the reaction vessel at specific times for product analyses. Head space and solution samples were removed from the reaction vessel using a syringe. The analyses were conducted using authentic samples which were co-injected to confirm the

identification of intermediate products with n-butanol as the internal standard. All samples were analyzed by HP 5890 Series II GC with HP 19395A sampler equipped with two columns by Restek corporation (Rtx-BAC1, ID 0.53 mm, 30-meter and RtxBAC2, ID 0.53 mm, 30-meter) and coupled with HP 3396 series II integrator. Mass spectra were run on a HP6890/HP-5973 GC/MS (EI) equipped with HP 7694 autosampler and DB-5 ID 0.32 mm, 60 meter column.

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Fenton's Reagent for Destruction of Methyl *tert*-Butyl Ether and Other Petroleum Hydrocarbons in Water

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Fenton's reagent is a potentially effective method of destroying MTBE and other petroleum hydrocarbons in water. Treatment of groundwater with 1% H_2O_2 and 5 mM Fe(II) at pH 3 destroyed >99.8% MTBE, >93.2% TPH, and >98.5% BTEX within 24 hours. Less than 0.01% of the MTBE, 5.1% of the TPH and <0.7% of the BTEX was volatilzed. The rates and amounts of O_2 and heat generated depended up the amounts of H_2O_2 and Fe(II) used, and must be taken into account when designing a treatment scheme.

Introduction

Fenton's reagent is an acidified mixture of hydrogen peroxide (H_2O_2) and ferrous iron (Fe(II)), whose exceptionally strong oxidizing ability was first reported by H.J.H. Fenton in 1894 *(1)*. It's ability to degrade a wide range of organic compounds, including benzene, toluene, ethylbenzene and xylenes (BTEX) and petroleum hydrocarbons, has generated significant interest in the environmental community *(2-6)*.

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The reaction mechanism by which Fenton oxidation occurs is not completely characterized, but it is generally believed that Fenton's reagent generates hydroxyl radicals (HO$^\bullet$) that react with organic substrates (R) in solution *(7)* [Eqn. 1-2]:

$$H_2O_2 + Fe(II) \rightarrow HO^\bullet + OH^- + Fe(III) \qquad \text{Eqn. 1}$$
$$RH + HO^\bullet \rightarrow R^\bullet + H_2O \qquad \text{Eqn. 2}$$
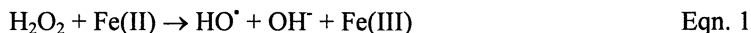
However, recent work by Watts et al *(8)* suggests non-radical species may be more important for some substrates or in the presence of soil. Ideally, oxidation can continue until substrate has been completely mineralized (converted to carbon dioxide).

As seen from Eqns. 3-8 *(7)*, the hydroxyl radical is non-selective and can be utilized by constituents other than the chemicals of concern (COCs). Note, too, that both H_2O_2 and Fe(II) can be regenerated. For these reasons, it is difficult to assign a stoichiometry to Fenton oxidation and to predict how much H_2O_2 and Fe(II) will be required to achieve the desired degree of removal of a specific organic compound.

$$H_2O_2 + Fe(III) \rightarrow Fe(II) + H^+ + HO_2^\bullet \qquad \text{Eqn. 3}$$
$$HO^\bullet + Fe(II) \rightarrow OH^- + Fe(III) \qquad \text{Eqn. 4}$$
$$HO_2^\bullet + Fe(III) \rightarrow O_2 + H^+ + Fe(II) \qquad \text{Eqn. 5}$$
$$H_2O_2 + HO^\bullet \rightarrow H_2O + HO_2^\bullet \qquad \text{Eqn. 6}$$
$$R^\bullet + Fe(III) \rightarrow Fe(II) + products \qquad \text{Eqn. 7}$$
$$2HO^\bullet \rightarrow H_2O_2 \qquad \text{Eqn. 8}$$
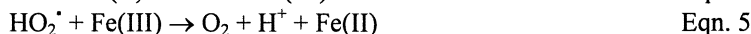
Other factors to consider when evaluating Fenton's reagent as a remediation option are the formation of oxygen gas (O_2), heat and iron floc. In addition to reacting with Fe(II) and Fe(III) [Eqns. 1, 3], H_2O_2 decomposes according to Eqn. 9. Based on this stoichiometry, 1 L of 1% H_2O_2 (v/v) will generate 4.5 L of O_2 at standard temperature and pressure (25°C, 1 atmopshere). The Fenton reaction is exothermic and thus can increase the temperature of the surrounding material. In the presence of H_2O_2, Fe(II) is rapidly oxidized to Fe(III) [Eqn. 1], which will precipitate as an iron hydroxide floc when the pH rises above about pH 5.

$$2H_2O_2 \rightarrow O_2 + H_2O \qquad \text{Eqn. 9}$$
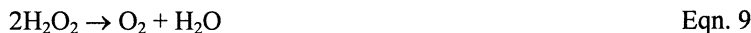
Treatability testing conducted by the authors has shown that Fenton's reagent can successfully destroy many types of organic compounds in water, including MTBE, BTEX, petroleum hydrocarbons, and chlorinated solvents. Most tests were conducted using site water and mild conditions (1-5% H_2O_2, 2.5-50 mM Fe(II)). This paper describes some of these tests and uses the data to

illustrate important issues associated with the full-scale *in situ* or *ex situ* implementation of Fenton oxidation technology.

Materials and Methods

Reagent grade ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was obtained from J.T.Baker. Fe(II) solution was prepared by dissolving $FeSO_4 \cdot 7H_2O$ in deionized water acidified to pH 2-3 with sulfuric acid such that the concentration of Fe^{2+} was 360mM. H_2O_2 (30%, A.C.S. reagent) was obtained from Fisher Scientific. Contaminated groundwater was obtained from various sites in California. Contaminanted soils were from Indiana. Although the soils were impacted with chlorinated hydrocarbons rather than petroleum hydrocarbons, the conclusions drawn from the data are unaffected. Sample locations and COCs are summarized in Table I.

Table I. Summary of Samples Tested.

Site Location	Matrix	COCs
Central California	Groundwater	MTBE, TPH, BTEX
Northern California	Groundwater	TPH, BTEX
Indiana	Groundwater, soil	Chlorinated hydrocarbons

Disappearance of Contaminants

Batch tests were performed in closed systems in order to determine whether losses were due to contaminant destruction or volatilization. Typically, contaminated water was acidifed to pH 3 with sulfuric acid and $FeSO_4 \cdot 7H_2O$ added such that the initial Fe(II) concentration was 5-500 mM. This water was then transferred to a Tedlar bag and 30% H_2O_2 added to obtain an initial concentration of 1-5% H_2O_2. In some cases, both H_2O_2 and Fe(II) were added to the Tedlar bag. During the transfer step, a sample was collected and analyzed for the COCs in order determine the initial concentration. Immediately after addition of H_2O_2, the Tedlar bag was connected to a second Tedlar bag in order to collect off-gases. The bags were placed on shaker table and gently mixed. After approximately 24 hours, the volume of gas was determined by measuring the volume of water filled bag displaced. An aqueous sample was collected and in some cases the pH was adjusted to pH ~7 to quench the Fenton reaction. Aqueous and gas phases were analyzed via EPA Method 8015, 8020, or 8260.

Rate of O_2 Formation/H_2O_2 Decomposition

The gases formed during Fenton oxidation are primarily O_2, though carbon dioxide and other compounds may also be present. The rate of gas formation is assumed to be equal to the minimum rate of H_2O_2 decomposition. (Because H_2O_2 also reacts with iron, the actually rate of H_2O_2 may be faster than the rate of O_2 formation. See Introdcution.) The rate of O_2 formation was measured by conducting the experiment as described above, except that the reaction vessel was an Erlenmeyer flask connected to an inverted graduated cylinder filled with water. The amount of water displaced by the gases was recorded periodically. The initial conditions were pH 3, 2.5 mM Fe(II), and 3-9% H_2O_2. In some cases, soil was added such that the liquid to soil ratio was 1.3:1.

Change in Temperature

An experiment was conducted in an Erlenmyer flask using a liquid to soil ratio of 1.3:1 and the following initial conditions: pH 3; 2.5 mM Fe^{2+}, and 3% H_2O_2. A thermometer was placed in the aqueous phase and the temperature monitored over time. The flask was not mixed in order to simulate the expected method of field appplication.

RESULTS

Disappearance of Contaminants

Central California Groundwater

A series of tests was conducted on groundwater from a site in Central California to determine the amount of Fe(II) and H_2O_2 that would be needed to remove MTBE and other contaminants in an *ex situ* reactor. The initial concentrations of H_2O_2 and Fe(II) used are shown in Table II. The results are given in Tables III and IV.

Complete removal of all contaminants from the aqueous phase was accomplished for Tests 2, 3, 6 and 7 (Table III). Gas collected during these tests contained only TPH-g and MTBE. A mass balance (Table IV) showed that the maximum amount of contaminant volatilized was 5.1% TPH, < 1.1% MTBE, and 1.0% BTEX, indicating that the primary mechanism of removal was destruction, not volatilization. (Note that the values in Table IV are conservative. When performing the mass balance calculations, contaminants not detected were assumed to be present *at* the detection limit. Because this assumption may

overestimate the contaminant concentrations, the percent volatilized or remaining in solution may be lower than reported, while the percent destroyed may be greater.)

Table II. Reaction Conditions for Determination of Dose Requirements in Groundwater from Central California.

Test	Total Volume, mL	Initial H_2O_2, %	Initial Fe(II), mM
1	450	1.1	0
2	450	1.1	4.8
3	450	1.1	48
4	450	1.1	480
5	450	3	0
6	450	3	4.5
7	450	3	45

Table III. Concentration of Contaminants in Aqueous and Gaseous Phases after Treatment of Groundwater from Central California[a].

Test	Time	Aqueous, µg/L			Gaseous, µg/L		
		MTBE	TPH	BTEX	MTBE	TPH	BTEX
1	Initial	7,100	2,200	95.7			
	Final	210[b]	220[b]	< 2.5[b]	n.a.[c]	n.a.	n.a.
2	Initial	6,200	3,000	300			
	Final	< 0.5	< 50	< 2.5	0.14	25	< 0.5
3	Initial	6,700	3,400	233			
	Final	< 0.5	< 100	< 2.5	0.48	10	< 0.5
4	Initial	5,900	3,700	326			
	Final	1,600	< 500	15.4	38	52	1.2
5	Initial	5,600	3,800	391			
	Final	72[b]	130[b]	< 2.5[b]	33	94	< 0.6
6	Initial	6,200	3,000	300			
	Final	< 0.5	< 50	< 2.5	1.1	< 10	< 0.5
7	Initial	6,700	3,400	233			
	Final	< 0.5	< 50	< 2.5	< 0.1	< 10	< 0.5

[a] All analytes measured via EPA 8260.

[b] Significant losses probably due to volatilization. See text.

[c] Not applicable, no gas produced.

Table IV. Mass Balance for Treated Central California Groundwater.

Test		MTBE	TPH	BTEX
2	% in Aqueous	< 0.01	< 1.7	< 0.7
	% Volatilized	0.01	5.1	< 0.8
	% Destroyed	*> 99.8*	*> 93.2*	*> 98.5*
3	% in Aqueous	< 0.01	< 2.9	< 0.6
	% Volatilized	0.03	1.5	< 0.6
	% Destroyed	*> 99.96*	*> 95.6*	*> 98.8*
4	% in Aqueous	27	< 13	4.7
	% Volatilized	1.8	3.9	1.0
	% Destroyed	*72.2*	*> 82.9*	*94.3*
6	% in Aqueous	< 0.01	< 1.7	< 0.7
	% Volatilized	0.07	< 1.4	< 0.5
	% Destroyed	*> 99.92*	*> 96.9*	*> 98.8*
7	% in Aqueous	< 0.01	< 1.8	< 0.6
	% Volatilized	0.02	< 4.1	< 1.8
	% Destroyed	*> 99.97*	*> 94.1*	*> 97.6*

Test 4, which used the highest iron dose (1% H_2O_2 and 500 mM Fe(II)), did not completely remove the contaminants. This was probably due to the vigorousness of the reaction, as evidenced by the extremely rapid formation of gas. Thus, it is likely that H_2O_2 decomposed to O_2 via Eqn. 3 and 5 instead of forming hydroxyl radicals that could react with the contaminants. In addition, the rapid formation of gas may have sparged some of the contaminants before oxidation could occur.

In Tests 1 and 5, which contained no iron, significant removal of most contaminants occurred. Possibly, iron in the groundwater could have served as the iron source. However, most of the removal can probably be attributed to sparging during sample collection. When the samples were adjusted to pH 7, residual H_2O_2 decomposed, causing pressure build-up in the sample vials. When the vials were opened to relieve the pressure, severe bubbling occurred (in a manner similar to opening a soda bottle). The bubbling presumably resulted in at least partial volatilization of some compounds. Because of these unquantifiable losses, no attempt was made to calculate a mass balance for these tests.

Several qualitative observations were made during the performance of Tests 1-7 and should be taken into account when designing a treatment system. The vigorousness of the Fenton reaction—that is, the amount of heat and gas generated immediately upon addition of H_2O_2 to the acidified, Fe(II)-containing groundwater—increased with increasing Fe(II) concentration and with increasing H_2O_2. Thus, in Tests 1 and 5, which contained no Fe(II), no noticeable

temperature change occurred and no bubbling or other signs of gas formation were observed. However, bubbling was seen with as little as 5 mM Fe(II) (Tests 2 and 6). The bubbling became more rapid as the amount of Fe(II) was increased to 500 mM (Test 4). In fact, the bubbling was so intense in Test 4 that a noticeable amount of gas was lost during the few moments required to connect the reaction bag to the gas collection bag. Increasing the amount of Fe(II) also increased the amount of heat generated. For example, although the temperature of the water in Tests 2, 3 and 6 did not appear to increase, the aqueous phase in Tests 4 and 7 became noticeably warm. In a test utilizing 3% H_2O_2 and 500mM Fe(II), the aqueous phase got hot (the reaction was so vigorous in this case, that the Tedlar bag ruptured and the test could not be completed). For a given Fe(II) concentration, increasing the initial H_2O_2 concentration from 1% to 3% also seemed to increase the vigorousness of the Fenton reaction, but the change was less extreme than increasing Fe(II).

Northern California Groundwater

Table V shows the results of testing Fenton's reagent on groundwater from a site in Northern California. Approximately 30% of each contaminant was volatilized, while 66-71% was destroyed. This is significantly different from the Central California groundwater (Table IV) in which < 5.1% of each contaminant was volatilzed and > 90% contaminant destruction was achieved. The reasons for this difference are uncertain but may be due to higher H_2O_2 concentration used in the Northern California tests. This higher concentration may cause a more vigorous reaction, which could result in increased volatilization. Alternatively, the Northern California groundwater may contain constituents that inhibit the formation of hydroxyl radicals, thereby hindering the Fenton reaction. In any case, these data clearly demonstrate the need for site-specific testing to determine the effectiveness and dose requirements.

Table V. Concentration of Contaminants in Aqueous and Gaseous Phases after Treatment of Groundwater from Northern California*.

	Aqueous, µg/L		Gaseous, µg/L		% Volatilized	% Destroyed
	Initial	Final	Initial	Final		
TPH	33,000	650	0	1,400	33	66
BTEX	20,800	446	0	760	29	71

*5% H_2O_2, 5 mM Fe(II)

Product Formation

Detailed product studies were not performed in any of these expeirments. However, in the investigation of Central California groundwater, t-butyl alcohol (TBA, a known degradation product of MTBE that may itself soon be regulated) was formed in Tests 1 and 5, which used only H_2O_2. As seen in Figure 1, the amount of TBA formed seems to be greater in Test 5 (3% H_2O_2) than in Test 1, (1.1% H_2O_2). Although the presence of TBA is real, the data must not be over-interpreted because the initial MTBE concentration differed in the two tests and because it is not known how much MTBE (or TBA) was lost due to volatization during sample collection (see above). The formation of TBA in H_2O_2-only tests is important because some applications of "Fenton's reagent" do not add Fe(II). Instead, they rely on iron naturally present in soil or water *(9, 10)*. Further testing in needed to understand the formation and fate of TBA in these situations.
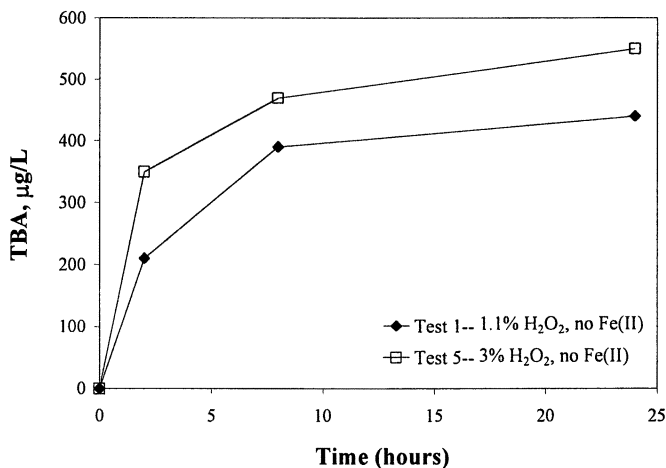
Figure 1. Formation of t-butyl alcohol during treatment of Central California groundwater with H_2O_2.

O_2 Formation/ H_2O_2 Decomposition

The rate of gas formation for various concentrations of H_2O_2 and in the presence and absence of soil is shown in Figure 2. The amount of gas generated

was proportional to the amount of H_2O_2 and was similar to the amount of O_2 expected based on the stoichiometry of Eqn. 9. Thus, increasing the concentration of H_2O_2 from 3% to 9% resulted in a three-fold increase in gas production (13L gas/ L soln. for 3% H_2O_2 versus 36 L gas / L soln. for 9% H_2O_2.).
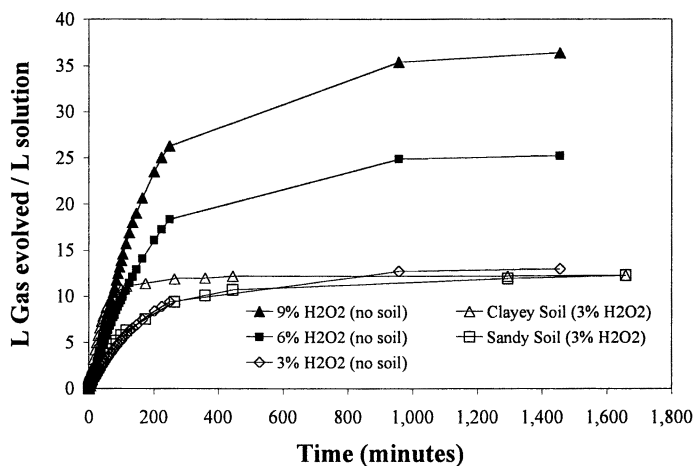
Figure 2. Gas Formation during Treatment with Fenton's Reagent. 2.5 mM Fe(II); 1.3:1 liquid:soil ratio.

The rate of gas formation also increased with increasing H_2O_2 concentration The initial rates (first 30 minutes) were 0.06 L gas/L soln-min , 0.11 Lgas/Lsoln-min, and 0.13 L gas/Lsoln-min for 3%, 6%, and 9% H_2O_2, respectively. In all three cases, approximately 72% of the gas produced was generated within 225 minutes (3.75 hours). This information is important for two reasons. First, the rate and volume of O_2 formed dictates what safety measures, if any, might be needed to manage O_2 during treatment. Second, the amount and rate of gas formation is directly proportional to the amount and rate of H_2O_2 consumption. Thus, if all of the gas is produced within 24 hours, it is reasonable to assume that all of the H_2O_2 has decomposed and that Fenton oxidation can no longer occur. (It must be noted that other factors may also affect the duration of the Fenton reaction. For example, increased pH due to alkalinity or soil buffering capacity may stop the reaction by removing Fe(II) from solution.)

The presence of soil can increase the rate of gas formation and H_2O_2 decompostion (Figure 2). In the case of clayey soil, 90% of the gas was formed within 116 minutes (2 hours). This is in sharp contrast to sandy soil or no soil, in

which 90% of the gas was formed within about 445 minutes (7.4 hours). The reason for this difference may be differences in the iron content of the soils (which was not measured) since soil iron could serve as an iron source and increase the rate of O_2 formation via Eqns 3 and 5. Alternatively, the increased rate of gas formation could be due to the greater surface area of the clayey particles compared to sand particles and the ability of the clay particles to remain suspended in the reaction solution. The data for sandy soil and no soil (3% H_2O_2) are almost identical, probably because the sand particles settled quickly, minimizing contact between them and Fenton's reagent.

Temperature

The initial change in temperature during a Fenton test utilizing 3% H_2O_2, 2.5 mM Fe(II), 2 L solution and 1.5 kg soil is depicted in Figure 3. The temperature rose 14°C in 30 minutes (25°C to 39°C) then remained nearly constant for at least 30 minutes more. While this change appears mild, it is important to note that the temperature will continue to rise if additional Fenton's reagent is added (as in an injection well) because the heat can not readily dissipate. Greater temperature increases may also be seen if higher H_2O_2 or Fe(II) concentrations are used. As discussed above (Disappearance of Contaminants, Central California Groundwater), increasing the concentration of either of these components increases the vigorousness of the Fenton reaction.
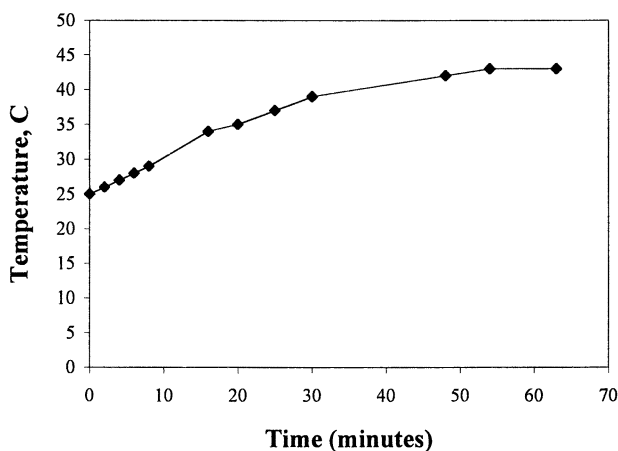
Figure 3. Increase in Temperature upon addition of Fenton's reagent to soil. 3% H_2O_2, 2.5mM Fe(II), 1.3:1 liquid:soil ratio.

Engineering Considerations

Fenton's reagent is a potenially useful method of remediating MTBE-contaminated water because it destroys MTBE rather than moves it from one medium (water) to another (air, activated carbon). In addition, Fenton's reagent destroys compounds commonly associated with MTBE, including BTEX and other petroleum hydrocarbons. Finally, the end products and by-products of Fenton oxidatin are potentially non-toxic and the technology can be applied either *in situ* or *ex situ*.

As with any remediation method, however, Fenton's reagent is not applicable at all sites. Tight formations are not suitable for *in situ* treatment because Fenton's reagent decomposes quickly and the reagent can not be dispersed, although research is being conducted on the use of ferric complexes overcome this limitation *(11, 12)*. Limestone formations are not suitable because Fenton's reagent is acidic and will dissolve the limestone, and treatment of soils with high organic content is generally not cost-effective. *Ex situ* treatment of hard water may also be difficult because carbonate can quench the Fenton reaction.

Specific issues related to *ex situ* and *in situ* treatment are discussed below.

Ex Situ

Because MTBE is highly mobile, a pump and treat system utilizing Fenton's reagent may be a suitable method for remediating MTBE-contaminanted groundwater. Water may be collected and treated periodically, or treated immediately upon extraction. In either case, provision must be made to acidifiy the water, add and mix reagents, and manage O_2. Post treatment steps to remove iron floc and adjust pH to near-neutral may also be needed prior to discharge.

In Situ

Because treatment solutions do not mix well with groundwater when injected into the subsurface, *in situ* remediation of MTBE poses a special problem compared to *in situ* treatment of other petroleum hydrocarbons. Unlike BTEX, gasoline or diesel fuel, MTBE does not sorb well to soils. Therefore, injection of treatment solution will tend to push the MTBE plume, rather than remediate it. This problem can be overcome by creating an *in situ* liquid barrier (Figure 4). In this scenario, a series of injection wells are installed at the downgradient end of the plume. Fenton' reagent is injected into the wells, creating a treatment zone. As the plume enters this zone, MTBE is destroyed.

Additional wells may be installed in the source area to treat other petroleum hydrocarbons and help push the MTBE plume toward the liquid barrier. Extraction wells may also be used to help control the plume. Other well configurations that force the MTBE plume to contact the treatment solution could also be effective.
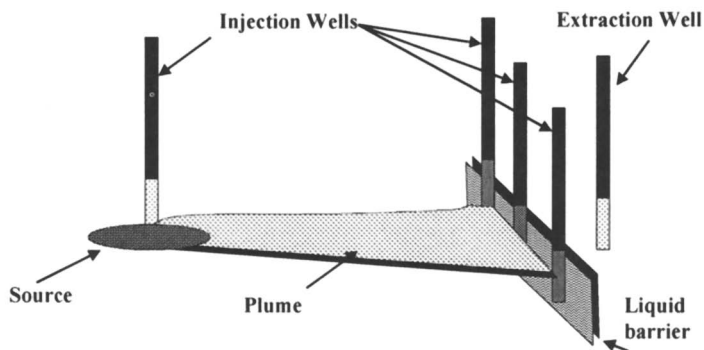
Figure 4. Conceptual Well Layout for In Situ Remediation of MTBE using Fenton's Reagent.

Conclusions

Fenton's reagent is a potentially effective method of treating MTBE andother petroleum hydrocarbons in water. Greater than 99% destruction of MTBE was achieved using the mild conditions 1% H_2O_2 and 5 mM Fe(II). The degree of contaminant removal and the optimal dose requirements for H_2O_2 and Fe(II) are site-specific. In addition, the H_2O_2 and Fe(II) concentrtions determine the amount and rate of O_2, heat and iron floc formation. These factors must be considered when designing a treatment strategy. Bench-scale or pilot-scale testing is recommended to address these issues prior to full-scale application of this technology.

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Chapter 14

Overview of Methyl *tert*-Butyl Ether Remediation and Treatment Strategies

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Due to an increase in the volume of MTBE added to gasoline over the past decade, environmental scientists and engineers are now compelled to re-evaluate the use of conventional remediation and treatment technologies for the removal of MTBE, its byproducts and other hydrocarbons from soil and groundwater at gasoline-impacted sites. This chapter is intended to summarize the highlights of a report recently prepared under the auspices of the California MTBE Research Partnership. The overall objective of this chapter is to provide a cursory overview of factors that should be considered when selecting MTBE remediation and treatment strategies. In addition, a review of the fate and transport of MTBE in the environment is provided, as well as a brief evaluation of demonstrated and emerging technologies for MTBE removal, lessons learned from case studies, and qualitative cost comparisons related to the use of some of these technologies.

Recent reports of the widespread occurrence of the fuel oxygenate methyl *tert*-butyl ether (MTBE) in groundwater at leaking underground storage tank (LUST) sites has led to a reassessment of conventional subsurface cleanup strategies. MTBE poses remediation challenges because of its unique physical and chemical properties relative to other gasoline hydrocarbons. It is highly soluble in water, does not sorb strongly to aquifer materials and exhibits a low tendency to volatilize from groundwater. Moreover, depending on gasoline release scenarios, MTBE could travel considerably beyond other gasoline constituents in subsurface environments thereby impacting larger volumes of groundwater. As a result, concerns have been raised regarding the feasibility of

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remediating MTBE-impacted soil and groundwater in an economic manner using technologies that have been traditionally employed at gasoline-contaminated sites.

The California MTBE Research Partnership recently completed a comprehensive report providing a critical evaluation of the effectiveness of existing and emerging remediation technologies in addressing cleanup challenges resulting from the presence of MTBE and its byproducts in soil and water (*1*). The Partnership's report provides extensive detail on conventional and emerging technologies. It therefore allows consultants, underground storage tank (UST) owners, regulators and other interested parties to address a wide range of UST cleanup problems at MTBE-impacted sites. The major findings of this report are presented here. In addition, this chapter includes a review of the environmental fate and transport characteristics of MTBE following accidental releases of MTBE-blended gasoline with an emphasis on the relevance of these characteristics on the selection and design of remediation strategies. Demonstrated *in situ* and *ex situ* remediation technologies are also evaluated on a comparative basis. In addition, a cursory overview of emerging technologies that can potentially replace or enhance conventional technologies is provided. Finally, remediation costs are discussed qualitatively in an effort to demonstrate how the presence of MTBE could affect overall remediation costs of gasoline-impacted sites. Detailed assessments of remediation and treatment costs and strategies for MTBE are available elsewhere (*1-2*).

Environmental Fate and Transport of MTBE

The starting point for evaluating an MTBE remediation strategy is to develop an understanding of the fate and transport of MTBE relative to other petroleum hydrocarbons following accidental gasoline releases. Gasoline aromatics, mainly BTEX compounds (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene), are of most concern due to their mobility and toxicity relative to gasoline aliphatics. MTBE is expected to co-exist with BTEX compounds near contaminant sources and at lagging edges of contaminant plumes. The fate and transport of MTBE in subsurface environments relative to BTEX compounds can be reasonably estimated by examining its chemical, physical and biological properties relative to BTEX compounds. While Table I summarizes key physical and chemical properties that govern the environmental fate and transport of the organic compounds in question, Table II illustrates how these properties impact MTBE's movement in various compartments of the subsurface (vadose zone, capillary fringe and saturated zone) relative to BTEX compounds. In addition to chemical-specific parameters (soil/water partition coefficient, Henry's constant, aqueous solubility, vapor pressure and density), hydrogeologic parameters (hydraulic conductivity, porosity, hydraulic gradient,

Table I. Selected Physical and Chemical Properties of Benzene (B), Toluene (T), Ethylbenzene (E), *o*-Xylene (*o*-X) and Methyl *tert*-Butyl Ether (MTBE).
(Reproduced from references 3-8.)

Physiochemical Property	Benzene	Toluene	Ethylbenzene	o-Xylene	MTBE
Specific gravity	0.88	0.87	0.87	0.88	0.74
Boiling point [°C]	80	111	136	144	54 - 55
Water solubility [mg/L]	1,780	535	161	175	43,000 - 54,300
Vapor pressure [mm Hg] @ 25°C	76 - 95	28	9.5	6.6	245 - 276
Henry's Law Constant [-]	0.23	0.27	0.34	0.21	0.018 - 0.026
Log K_{oc}[a]	1.2 - 2.2	1.6 - 2.3	2.0 - 3.0	1.7 - 1.8	1.0 - 1.1
Log K_{ow}[b]	1.6 - 2.2	2.1 - 2.8	3.2	2.8 - 3.1	1.2

[a] K_{oc} is the organic carbon based partition coefficient

[b] K_{ow} is the octanol water partition coefficient

Table II. Zones of Migration and Controlling Properties or Parameters

Zone	Controlling Parameter	MTBE Behavior as Parameter Increases	Controlling MTBE Property	Resulting MTBE Behavior relative to BTEX
Surface	Vol. % MTBE in gasoline	Slower time to 99% volatilization	Vapor pressure	More rapid volatilization
Vadose	Soil moisture content	Less volatilization	Vapor pressure	More rapid volatilization
Capillary Fringe	Recharge, soil porosity	Less residual	Henry's Constant, carbon partition coefficient	Faster dissolution
Saturated	Horizontal and vertical gradient, velocity	Longer, wider, deeper plume	Solubility, biodegradability, carbon partition coefficient	Less retardation, less biodegradation

fractional organic carbon content of the soil, microbial density and reduction-oxidation conditions) also influence relative rates of transport. Based on a review of MTBE's properties relative to BTEX compounds, the following conclusions and implications toward remediation can be made:

- The fraction of MTBE in gasoline varies regionally and seasonally (Table III). MTBE's pure component solubility and fraction in gasoline are much higher than those for benzene. This could theoretically result in a more rapid dissolution of MTBE from the source area relative to benzene (9). Furthermore, due to its chemical properties, MTBE sorbs poorly to aquifer materials (10). It therefore exists predominantly in the dissolved phase suggesting that groundwater-flushing technologies should be effective for MTBE removal from groundwater aquifers. MTBE's higher solubility than that of BTEX compounds suggests that groundwater-flushing technologies could be more effective for depleting MTBE than BTEX from source areas.
- MTBE has a much higher vapor pressure than BTEX compounds suggesting that vapor extraction technologies could be effective for removing MTBE from dry soils relative to BTEX compounds.
- MTBE's low sorption potential suggests that *ex situ* adsorption technologies (granular activated carbon, resins) are likely less efficient for removing MTBE from water relative to BTEX compounds.
- MTBE has a lower Henry's Constant than BTEX compounds suggesting that air stripping is likely to require a greater air to water ratio to achieve MTBE removal efficiencies similar to those for BTEX.
- MTBE is more difficult to biodegrade than BTEX compounds due to the high energy required by microorganisms to cleave the ether bond, and the resistance of the branched carbon structure to microbial attack (11). MTBE plumes are therefore likely to migrate past BTEX plumes given MTBE's higher mobility and lower tendency to biodegrade naturally relative to BTEX compounds (12-13).
- MTBE has a low octanol/water partition coefficient suggesting that it is not likely to bioaccumulate in plants and other organisms.

To verify the conclusions drawn regarding the fate and transport of MTBE relative to other gasoline components and to provide a framework for developing MTBE remediation strategies, it is useful to review MTBE and BTEX concentration data from actual field studies. Recently, plume studies were conducted in three states (California, Florida, and Texas) to determine the apparent distribution of BTEX and MTBE plumes (14-17). Figure 1 represents a compilation of data from several hundred benzene plumes and approximately 130 MTBE plumes. The results of these studies somewhat conflict with how one might expect an MTBE plume to behave based solely on MTBE's physical and chemical properties. Based on its properties, MTBE is expected to move at the

Table III. Oxygenated Fuels Facts

	Oxyfuel	Reformulated Gasoline (RFG)	California Air Resource Board Fuel (CARB)
Oxygen Weight %	2.7%	2.0%	1.8% - 2.2%
MTBE Volume %	15%	11%	Variable
First Documented Use	Winter 1992-1993	Jan. 1, 1995	Jan. 1, 1995
Use in California	-	All year Ozone non-attainment areas	All year All other areas
Use in 17 other states	Wintertime CO non-attainment areas	All year Ozone non-attainment areas	-
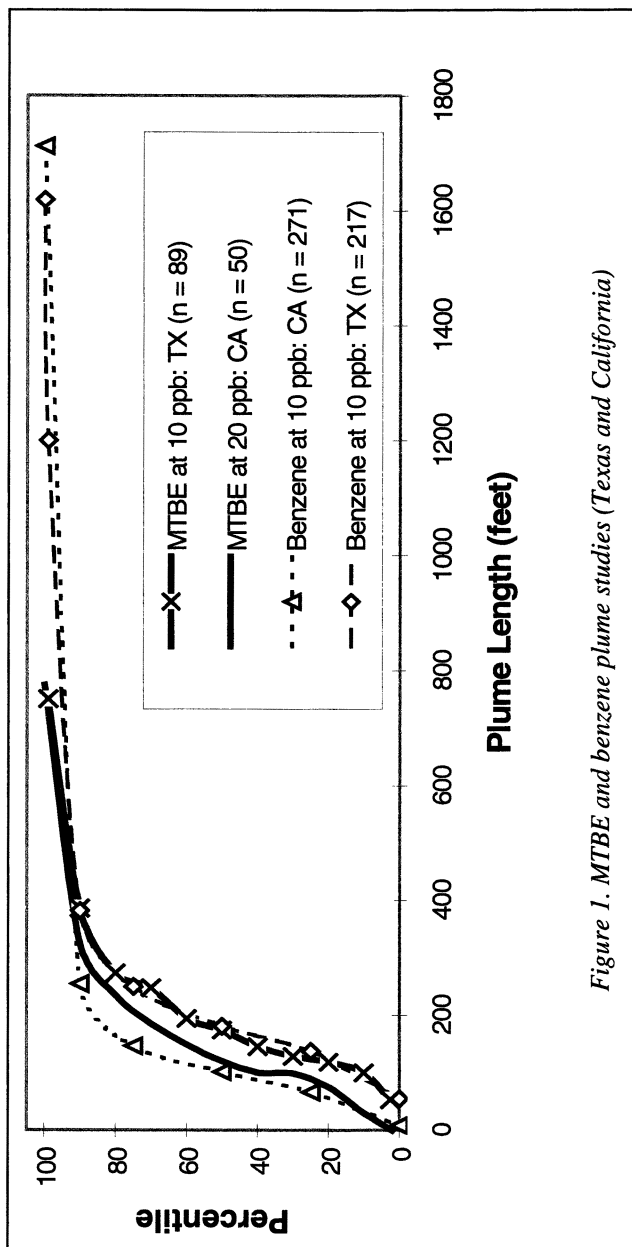
Figure 1. MTBE and benzene plume studies (Texas and California)

speed of groundwater with little or no retardation. However, most of the studies reviewed suggest that MTBE plumes neither elongate indefinitely as predicted, nor do they span substantially longer distances than BTEX plumes (Figure 1). These studies suggest that, depending on gasoline spill history and on site geology and hydrogeology, MTBE plumes could in some cases stabilize at a fixed distance from the source. The data presented in Figure 1 are mostly from sites with relatively recent spills. It is therefore possible that MTBE plumes at these sites did not have sufficient time to elongate significantly beyond the BTEX constituents. The implications of Figure 1 are significant because they indicate that the relative volume of groundwater requiring remediation at LUST sites following the addition of MTBE to gasoline does not drastically change immediately after a spill. Therefore, if active remediation is rapidly implemented following an accidental release of MTBE-blended gasoline, the incremental cost impacts associated with the presence of MTBE can be minimized. Alternatively, as remediation and/or plume containment are delayed, MTBE plumes could migrate rapidly thereby increasing both site characterization and remediation costs.

In summary, an understanding of MTBE's physical and chemical properties can be useful in selecting effective remediation strategies at MTBE-impacted sites (Table IV). Furthermore, a rapid response following a spill of MTBE-blended gasoline is essential to minimize site characterization and remediation costs, as well as costs associated with off-site impacts.

MTBE Treatment and Remediation Technologies

Following a theoretical understanding of how MTBE and BTEX compounds behave in the environment, it is critical to adequately define the extent of contamination at gasoline release sites through a thorough site investigation and the development of a site conceptual model. The establishment of acceptable remedial objectives follows for all stakeholders. Only then can applicable and appropriate technologies be identified to achieve these goals (Table V). Although traditional approaches for site investigation and corrective action at gasoline release sites are applicable and useful at MTBE-impacted sites, some issues are unique to sites with MTBE contamination. Such sites could require more extensive site investigation due to the migration of MTBE plumes beyond the BTEX constituents and the need for vertical characterization of MTBE distribution (18). In addition, there could be a need for greater residual product removal at MTBE-impacted sites due to the potential for continuous slow release of MTBE from the residual product. Therefore, MTBE-impacted sites could require more intense remediation in the source area relative to BTEX-only sites. A guide for characterizing subsurface releases of gasoline containing MTBE is available elsewhere (19).

Table IV. Selection of a Remediation Strategy

Chemical Property	Remediation Strategy that Capitalizes on a High Value of Property
Biodegradability	Enhanced *In Situ* Bioremediation
Henry's Constant	Steam Stripping, Air Sparging
Solubility	Air Sparging, Enhanced *In Situ* Bioremediation
Oxidation Potential	*In Situ* Chemical Oxidation
Vapor Pressure	Soil Vapor Extraction, Multi-Phase Extraction

Table V. Relative Difficulty for Remediating MTBE and BTEX Contamination

More Difficult	Less Difficult
• Slower intrinsic bioremediation • Plume characterization uncertainty • Minimal retardation (more rapid response required) • Potential for detached plumes (although rare) • Potential for thicker, deeper plumes • Perception of complexity	• Slower time required for flushing (air or water) • Higher vapor pressure

Following site characterization and the development of a conceptual model, a number of *in situ* and *ex situ* technologies can be used to effectively remediate MTBE-impacted sites including pump-and-treat or groundwater extraction, soil vapor extraction, multi-phase extraction, *in situ* air sparging, *in situ* bioremediation, *in situ* chemical oxidation and natural attenuation (Figure 2). Most of these technologies have been shown to be successful in partially or fully remediating MTBE-impacted sites. In addition, several non-conventional technologies have shown promise of success for MTBE removal from contaminated environments. A very brief overview of conventional and emerging technologies is presented below. Detailed information is available elsewhere (*1-2*).

Pump-and-Treat

Based on the information evaluated, pump-and-treat appears to be successful in removing MTBE from groundwater. The enhanced solubility of MTBE relative to BTEX suggests that MTBE subsurface concentrations can be significantly reduced with fewer pore volumes of extracted groundwater. Furthermore, due to MTBE's relatively low sorption potential, dissolved-phase MTBE concentrations are much less likely to rebound than BTEX following cessation of pumping activity. However, due to the physiochemical properties of MTBE, MTBE plumes may extend much greater distances than BTEX plumes. As a result, the extent and capacity of groundwater pumping systems may need to be expanded for MTBE remediation relative to BTEX-only systems. Once contaminated groundwater has been pumped to the surface, established water treatment technologies, including air stripping and granular activated carbon, are capable of removing MTBE from groundwater to acceptable levels for discharge of the treated water (*2, 20*). Several processes including pulsed and adaptive pumping can be used to optimize pump-and-treat performance (*21*). Studies have demonstrated that these pumping techniques significantly reduce the time required for site remediation.

Soil Vapor Extraction (SVE)

The success of SVE at removing MTBE from gasoline-contaminated soils has been documented by a number of studies (*2*). When site characteristics are favorable, SVE can be effective in removing MTBE relative to BTEX compounds in the vadose zone even if contaminants are present as residual or free-phase products. The combination of SVE and pump-and-treat, designated as multi-phase extraction (MPE), allows for the remediation of both soil and groundwater with higher efficiencies than the separate application of each of

	Phase Transfer	Transformation / Destruction
Ex Situ	• Air Stripping • Activated Carbon • Resins • Membranes • Solvent Extraction	• Advanced Oxidation • Biological Filtration • Thermal/Catalytic Oxidation

In Situ	• Soil Vapor Extraction
	• Air Sparging
	• Groundwater Pumping
	• Multi-Phase Extraction
	• Steam Stripping
	• Phytoremediation
	  (Transpiration/Adsorption)
		• Chemical Oxidation
		  - Hydrogen Peroxide
		  - Ozone
		  - UV
		• Bioremediation
		  - Intrinsic or Engineered
		  - Aerobic or Anaerobic
		  - Primary or Cometabolic
		• Thermal Desorption
		• Reactive Barrier Walls
		• Phytoremediation

Figure 2. Potential MTBE remediation and treatment technologies

these technologies. Recent field studies have demonstrated the effectiveness of MPE at MTBE-impacted sites (22). As a result, the use of MPE for the removal of MTBE and BTEX from subsurface environments has increased in the last several years.

In Situ Air Sparging (IAS)

The effectiveness of IAS for the remediation of gasoline-contaminated sites is well established (23-26). IAS is promising for MTBE remediation despite the apparent slow rate of MTBE biodegradation and its low Henry's constant. This is because MTBE is primarily present in the dissolved-phase at gasoline-contaminated aquifers. Therefore, if the hydrogeology of the site is amenable to air sparging, it is likely to be effective for MTBE removal. Recent field studies have shown that IAS effectively reduced MTBE concentrations over a period of two years at seven of ten sites tested.

In Situ Bioremediation

Bioremediation involves the use of microorganisms to either destroy or immobilize contaminants. *In situ* bioremediation of soil and groundwater contaminants has achieved a measure of success in both field tests and commercial-scale cleanups for gasoline contamination. Field applications of *in situ* bioremediation at MTBE-impacted sites are discussed in detail in another chapter of this book and elsewhere (27-28). Laboratory studies indicate that a number of cultures from diverse environments can either partially degrade or completely mineralize MTBE. Preliminary results from field studies using *in situ* bioaugmentation and/or oxygen injection at Port Hueneme (29) and at Vandenberg Air Force Base (30) suggest that bioremediation has a strong potential for success at MTBE-impacted sites. *In situ* bioremediation strategies could involve direct metabolism, cometabolism, bioaugmentation or some combination thereof.

In Situ Chemical Oxidation

Chemical oxidation relies on the use of ozone, hydrogen peroxide or other chemical agents to either directly react with MTBE, or to form hydroxyl radicals which can then attack MTBE. For organic compounds, the effectiveness of *in situ* oxidation is limited by oxidant delivery in complex hydrogeologic conditions, competition from hydroxyl radical scavengers and safety issues associated with the transport and application of oxidants. *In situ* chemical

oxidation has been used in some cases at MTBE-impacted sites with modest success (21). More studies are needed to identify variables that impact the effectiveness of *in situ* chemical oxidation for MTBE removal.

Monitored Natural Attenuation

Natural attenuation encompasses a number of physical, chemical and biological processes that reduce, restrict and/or eliminate contaminant migration in subsurface environments (31). Natural attenuation as a remediation strategy is likely less effective for MTBE removal relative to BTEX compounds due to MTBE's low retardation factor and slow rate of biodegradation, especially under anaerobic conditions. MTBE attenuation rates have been shown to be site dependent and can be expected to vary with time and position across a single plume. In addition, MTBE bioattenuation rates are in most cases greatly influenced by the gasoline release history at the site.

Emerging Technologies

In addition to the MTBE-demonstrated technologies discussed above, several emerging technologies have shown some promise for the remediation of sites and treatment of water contaminated with MTBE. Furthermore, emerging techniques and process enhancements can be implemented together with a demonstrated technology for improved efficiency and/or reduction in remediation timeline and costs. Emerging technologies for MTBE removal include *ex situ* technologies such as advanced oxidation processes (AOPs) and synthetic resin sorbents as well as *in situ* technologies such as thermal processes.

Laboratory scale demonstrations indicate that both AOPs and synthetic resins show promise for successful MTBE removal from water (2). AOPs include O_3/H_2O_2, O_3/UV, $H_2O_2/MP-UV$, High Energy Electron Beam Irradiation (E-beam), TiO_2-catalyzed UV, Sonication/Hydrodynamic Cavitation and Fenton's Reaction. Several field evaluations of O_3/H_2O_2 systems indicate that AOPs can achieve MTBE removal rates exceeding 99%. Some of the research gaps involving the use of AOPs for the treatment of MTBE-contaminated water include the formation and fate of oxidation byproducts, non-selective radical oxidation, radical scavenging and bromate formation.

Limited field data are available on the effectiveness of resins for MTBE removal. Laboratory studies indicate that two synthetic resins are promising candidates for MTBE removal from water (2). Studies to evaluate the effect of water quality parameters on MTBE removal efficiency by resins are ongoing.

In situ emerging technologies for MTBE removal from subsurface environments include thermal processes such as six-phase heating, radio

frequency heating and dynamic underground stripping. Thermal processes can be used to enhance SVE, MPE and *in situ* bioremediation. In addition, some thermal processes, mainly dynamic underground stripping which involves steam injection and vacuum extraction, have been shown to be very successful in achieving nearly complete removal of residual gasoline in the source area of gasoline-contaminated sites (*32-33*). This and other *in situ* thermal technologies have not been used yet to remediate MTBE-contaminated aquifers but are expected to be successful, especially in removing LNAPL from subsurface environments.

Overview of MTBE Case Studies

Case studies are needed for a clear understanding of the effectiveness of remediation strategies and technologies at MTBE-impacted sites. Five case studies were carefully reviewed (*1*). Case study sites were chosen based on several criteria: (a) contamination by MTBE-blended gasoline; (b) remediation has been taking place for over a year; (c) availability and adequacy of groundwater and soil data, and remediation system performance analyses; (d) availability of design and operational information for the remediation systems; (e) availability of capital, and operation and maintenance costs.

The case studies reviewed involved a range of applicable remediation technologies. In several cases, groundwater extraction was used, either as a singular remediation technology or in combination with other *in situ* technologies such as SVE. In these cases, the extracted groundwater was treated either by air stripping or granular activated carbon. A review of these studies indicated that MTBE concentrations in the extracted water were shown to decline at all sites following pumping activities. Very little rebound of MTBE levels was detected during the first few years of pumping whereas rebound is commonly expected with other gasoline components. Air stripping was used as a primary treatment method for the extracted groundwater at most of the sites evaluated. The case studies investigated revealed that air stripping is a robust technology capable of achieving high MTBE removal efficiencies. However, if off-gas treatment is needed, remediation costs can significantly increase. Furthermore, low effluent treatment goals significantly impacted costs since the operation of multiple air stripping towers in series was required in some cases to achieve target cleanup levels.

Granular activated carbon (GAC) was used to treat extracted groundwater at two of the field studies evaluated. Although GAC applications were costly, the use of GAC for MTBE removal continues to take place because of process simplicity.

Soil vapor extraction was utilized at four of the five case study sites either alone or in combination with groundwater extraction. The presence of MTBE

did not appear to affect the application of SVE. Based on field results, SVE is an effective remediation method for MTBE.

Vapor treatment was used at four of the case study sites to treat the vapors from SVE systems and air strippers. GAC was found to be ineffective for off-gas streams with high concentrations.

The costs associated with the different remediation strategies at MTBE-impacted sites are highly site-specific making generalizations on unit costs difficult. Several factors greatly influence cost estimates including the presence of other contaminants, range of hydrocarbon concentrations, location of contaminants of concern, hydrogeological parameters at the site, size of the impacted area and target cleanup concentrations. Three accidental release scenarios of MTBE-blended gasoline were evaluated on a comparative basis including a "young" shallow release, an "older" large plume and a large vadose zone release. Costs for MTBE and BTEX remediation were calculated from capital and operating cost information provided by technology vendors. Additional costs were added for site work, piping, valves, and electrical work needed to install the system (if applicable), contractor profit, engineering and contingency. For each of the scenarios, the vendors were asked to provide costs for BTEX and MTBE cleanup as well as BTEX-only cleanup. Each vendor assumed that the "BTEX and MTBE cleanup" plume size was identical to the "BTEX-only cleanup" plume size for each scenario. Therefore, the cost estimates are more accurate for sites with younger MTBE releases and older BTEX releases where MTBE plume sizes are often equal to or less than BTEX plumes. Despite this limitation, the assumption of equal plumes sizes allowed a unit plume cost comparison. The vendors were also asked to estimate the time required for complete remediation.

In comparing the results from the three scenarios, air sparging (AS) combined with SVE was found to be the most cost effective remediation technology at MTBE-impacted sites. As the volume of contaminated groundwater increased, the cost effectiveness of AS/SVE was shown to decrease. However, compared to other available technologies, this appears to be relatively the lowest in cost. Oxygen addition was found to be cost-effective for plume management assuming that biodegradation is occurring. However, because of the uncertainty associated with MTBE biodegradation, this approach should be evaluated on a site-specific basis.

Conclusions

Demonstrated remediation and treatment technologies are available that can remove MTBE from soil and groundwater to regulatory limits, assuming that these limits are technically practicable in the given geological setting. These technologies include air sparging, pump-and-treat, multi-phase extraction and soil vapor

extraction, most of which have been widely applied at gasoline-contaminated sites prior to the widespread use of MTBE in gasoline. Whether these technologies can meet regulatory or risk-based cleanup levels is a highly site-specific issue. Conventional technologies appear to be reasonably effective at removing MTBE from soil and groundwater relative to BTEX removal from environmental media. The successful removal of NAPL sources does not appear to be impacted by the presence of MTBE. In addition to traditionally used technologies at gasoline-contaminated sites, emerging technologies or modifications to existing technologies can greatly reduce the life cycle remediation costs at MTBE-impacted sites.

Changes in remediation costs for MTBE/BTEX relative to BTEX-only contaminated sites can be estimated by first taking into consideration contaminant plume sizes. The presence of MTBE in groundwater could increase site characterization costs should MTBE migrate substantial distances beyond the BTEX constituents in gasoline-contaminated groundwater. MTBE could follow preferential pathways and is more likely to migrate vertically than BTEX compounds when vertical gradients caused by pumping or recharge exist.

Costs of MTBE remediation and treatment could also increase due to other factors. First, MTBE does not appear to undergo rapid natural biodegradation although plume study results and some detailed research investigations (29-30) indicate that MTBE, in the absence of BTEX compounds, can be biodegraded by naturally occurring microorganisms. Because intrinsic biodegradation rates have been observed to be low, the number of sites where monitored natural attenuation can be used as the sole remedial action is limited. Thus, the number of LUST sites requiring active remediation could increase due to the presence of MTBE. The incremental cost compared to BTEX only sites on a national basis will be substantial if remediation of releases of gasoline containing MTBE is delayed. Where remediation is required to meet risk-based requirements or regulatory mandated cleanups, existing technologies are capable of effectively removing MTBE from soil and groundwater. Rapid detection and remediation of gasoline releases from USTs is essential to reduce the incremental increase in life cycle remediation costs at MTBE-impacted sites.

In summary, technologies are either available or under development that are capable of meeting cleanup objectives at most MTBE-impacted sites. Further field studies are needed to confirm that MTBE remediation problems can be resolved at a reasonable cost.

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Chapter 15

Evaluation of the Adsorption Process for the Removal of Methyl *tert*-Butyl Ether from Drinking Water

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Methyl *tert*-butyl ether (MTBE) is a fuel additive used as a replacement for lead and an octane booster (*1*). It was first used in United States in late 1970s and has since become the oxygenate of choice due to economic and supply considerations (*2*). By 1998, MTBE has become the fourth-highest produced organic chemical in the United States (*3*). The widespread use of MTBE, combined with its chemical and physical characteristics, has resulted in its detection in ground and surface waters in many urban regions throughout the country (*4, 5*). *The Report of the Blue Ribbon Panel on Oxygenates in Gasoline* (*6*) stated that between 5 and 10% of community drinking water supplies in high MTBE use areas show at least detectable concentrations of MTBE. California Department of Health Services (CAL-DHS) has set primary and secondary drinking water standards of 13 and 5 µg/L, respectively.

Removal of MTBE from affected drinking water sites can be achieved through several water treatment processes such as air stripping, advanced oxidation, membrane separation, and sorption (*7*). This paper will briefly review different water treatment options and their relationship to the use of adsorption

processes. This paper will then develop cost data for adsorption processes, which can be used in a cost effective manner, alone, as a final cleanup or after another treatment such as advanced oxidation processes.

Air Stripping

Air stripping can remove more than 99% of MTBE and trichloroethene from groundwater (2). However, air stripping of MTBE requires high air-to-water ratios because the compound is highly water soluble with a low Henry's law constant. Sevilla et al. (8) reported over six times higher air-to-water ratio is required for the treatment of MTBE contaminated waters compared to other petroleum hydrocarbons. Thus, the use of air stripping as a sole process for removing MTBE may not be cost effective. In addition, the process involves mass transfer from water to air phase, producing contaminated air stream that may require further treatment, such as sorption by activated carbon, depending on local air emissions regulations (2).

Advanced Oxidation Processes

During advanced oxidation processes (AOPs), ozone, UV light, hydrogen peroxide (H_2O_2), metal oxides (such as titanium dioxide, TiO_2), Fenton's reagent (iron sulfate and H_2O_2 in an aqueous solution at pH = 2.5), and ultrasonic cavitation, or in combination, to produce hydroxyl radical ($OH^•$). MTBE could react with hydroxyl radical and form formaldehyde and *tert*-butyl alcohol (TBA). Vel Leitner et al. (9) indicated that effective removal of MTBE of greater than 80% from water can be achieved using peroxone (ozone/peroxide) oxidation. Liang et al. (10, 11) completed an initial pilot plant study of ozonation and peroxone treatment of MTBE under optimum conditions for taste and odor control. The results for two MTBE concentrations (18 to 76 µg/L) indicated peroxone with 4 mg/L of ozone and 1.3 mg/L of hydrogen peroxide at pH 8.3 could achieve about 80% removal for waters from the State Project and Colorado River. However, bromate is a by-product of this process and exceeded the 10 µg/L MCL. Ozonation alone was also effective at longer detention times (12). Thus, AOPs are a viable option with polishing of any MTBE remaining by GAC, if the bromate is controlled. GAC polishing is needed to assure that any residual MTBE or its breakdown products are not released into the drinking water. In addition, GAC will remove biodegradable organic carbon produced by AOPs, which should be removed before drinking water is distributed to prevent bacterial growth in the distribution system.

Membrane Processes

Although nanofiltration (NF) and reverse osmosis (RO) have the potential to remove MTBE from water, they have not been as widely studied as aeration, AOPs, and adsorption. The use of membrane processes, especially RO, in general water treatment applications is not cost effective unless other treatment requirements are included (7). On the other hand, microporous hollow fiber membranes (HFM) have been successfully used to strip various compounds from water (2). HFM can improve the mass transfer rate of MTBE from water to air, as contaminated water is pumped through the lumen side of bundled microporous fibers while a vacuum is drawn counter-currently on the outside of the fibers. Compare to air stripping, HFM allows for more efficient transfer of volatile compounds from aqueous to gas phase. Studies have shown that mass transfer of volatile organics could be an order of magnitude greater than achievable by packed tower aeration when using HFM (2).

Adsorption

Granular activated carbon (GAC) and powder activated carbon (PAC) have been widely used for control of taste and odor in drinking water (13, 14, 15). The application of PAC is more flexible and requires less capital costs than GAC. However, for long periods of activated carbon application, it may be more economical to use GAC. A well designed and maintained GAC column can be operated efficiently for several years to remove low to moderate concentrations of contaminants (16).

Adsorption is a proven technology for treating water contaminated with many taste- and odor-causing organics and synthetic organic chemicals (2, 17). GAC could be used alone or after any type of AOP to remove residual MTBE, oxidation products of MTBE (e.g. TBA), and biodegradable organic carbon produced by AOPs (e.g. aldehydes).

Treatment Options

Many treatment options are described above. However, if any of them are used in a cost effective manner, GAC treatment may be included – if not alone, then as a final cleanup after another treatment such as AOPs or even applied as an adsorbent for the gaseous phase after air stripping. Therefore of all the treatments knowledge about the cost effectiveness of GAC is needed to evaluate any comparisons. The remainder of the paper will evaluate the cost effectiveness of the GAC adsorbents of choice in a column mode.

Objectives

The present study investigated the cost and effectiveness of the adsorption process, both as a sole process for removing MTBE from drinking water to taste and odor threshold levels (<5 μg/L) and as a polishing process after the application of AOPs. Various GACs were investigated. The effects of breakdown products of MTBE (e.g. TBA) and background natural organic matter (NOM) on the adsorption process were studied. A comparison of isotherms with rapid small-scaled column tests (RSSCTs) were performed to demonstrate the discrepancy between the results generated by equilibrium (isotherms) and dynamic (RSSCTs) tests.

Results and Discussions

Figure 1 shows the results of linear regressions of the isotherm data after log-transformation for six GACs used with MTBE in organic-free water (7). The isotherm is a batch reactor method that is used to assess the equilibrium adsorption capacity of the adsorbents for the solute of interest, and is usually run in batch reactors with different ratios of carbon dose to initial component concentration. It establishes the equilibrium adsorption capacity, or solid-phase concentration for a specific compound as a function of the liquid-phase concentration. The isotherms were conducted with 1,000 μg/L of influent MTBE. The results show the coconut GAC (Calgon GRC-22) had the highest equilibrium adsorption capacity for MTBE, followed by peat and bituminous I, respectively. The data for these adsorbents also agreed with the Freundlich model, particularly for the case of coconut GAC (with $r^2 > 0.95$). The coconut GAC was further investigated with MTBE, NOM, and TBA in groundwater from Santa Monica, California (total organic carbon [TOC] = 0.5 mg/L). The effects of NOM and TBA on the equilibrium capacity of coconut GAC are shown in Figure 2 (7). Significant reductions in equilibrium adsorption capacity were observed by the addition of NOM and/or TBA, with the competitive effect of NOM on MTBE adsorption greater than TBA since the equilibrium adsorption capacity with TBA in organic-free water is higher than in the presence of NOM. The isotherms show the coconut GAC to be the most cost-effective adsorbent for use as a sole process and as a polishing process after advanced oxidation; however, competitive adsorption of TBA and NOM in the background competes with the adsorption of MTBE to coconut GAC (7).

Consequently, further evaluation of the most cost-effective adsorbent, the coconut GAC was conducted using two candidate coconut GACs, the PCB (Calgon) and CC-602 (U.S. Filter) GAC in both organic-free water and in two groundwater sources and a surface water source. The water quality parameters
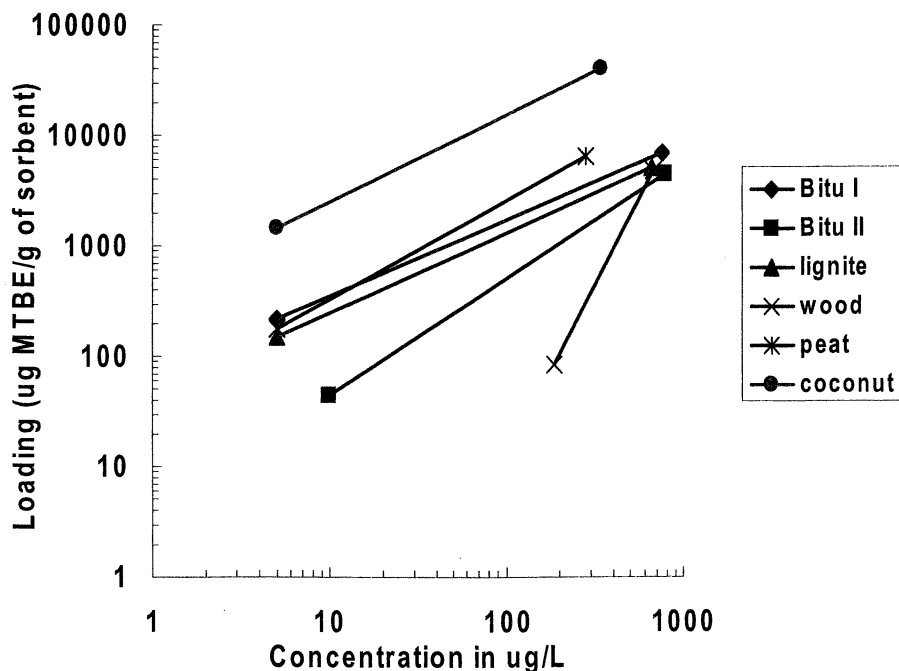
Figure 1. Isotherm of 6 GACs with 1,000 µg/L influent MTBE in organic-free water. Best fit line is shown for clarity. Actual data points are not shown (Adapted with permission from reference 7. Copyright American Water Works Association).
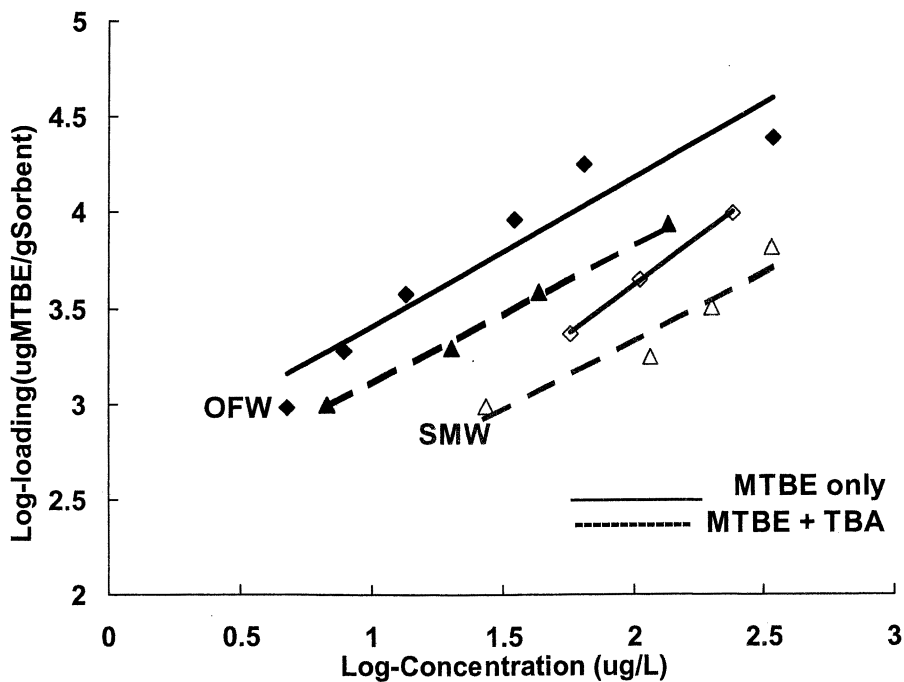
Figure 2. Isotherm of coconut GAC (GRC-22) in organic-free water (OFW) or in Santa Monica water (SMW) with MTBE (1,000 µg/L) or MTBE and tert-butyl alcohol (100 µg/L) (Reproduced with permission from reference 7. Copyright American Water Works Association).

for the natural water sources are shown in Table I. Each of these water sources has different sources of NOM; i.e. South Lake Tahoe Utility District [SLTUD] (pine forest), Arcadia Well Field [ARWF] (groundwater from desert flora and urban runoff), and Lake Perris [LP] (Colorado River Water stored in a lake environment which changes with the season and nutrient levels).

Table I. Analysis of Water Quality Parameters

Water Source	pH	Conductivity (μmhos/cm)	TOC (ppm)	UV_{254} Abs	$SUVA^a$	MTBE (μg/L)	TBA (μg/L)
ARWF	7.8	1130	1.0	0.008	0.8	<1	<1
SLTUD	7.9	77	0.2	0.004	2.0	<1	<1
LP	8.5	640	3.2	0.068	2.1	5-10	<1

NOTE: ^{a} SUVA = Specific UV Absorbance (UV_{254} Absorbance x 100/TOC)
SOURCE: Data are from Reference 26

Studies have used TOC or dissolved organic carbon (DOC) as surrogates for the quantification of NOM (21, 24, 25). However, since the type and adsorbability of NOM in natural waters may vary, it is apparent that the measured TOC or DOC concentrations alone and UV_{254} absorbance normalized TOC (SUVA) may not always be an accurate indicator of the impact of NOM. In the present study, the performance of the two coconut GACs in removing MTBE from three natural water was investigated and attempts were made to correlate the TOC content to GAC performance parameters (e.g. carbon usage rate). The TOC concentration of the water sources ranged from 0.2 mg/L (low) to 3.2 mg/L (medium) for groundwater from SLTUD and for surface water from LP, respectively. In addition, a SUVA of less than 3 usually indicate a more hydrophilic TOC than a SUVA of over 5.

Figure 3 is a plot of isotherms of the two coconut GACs in both organic-free water and in the three natural water sources (26). The isotherms were conducted with 1,000 μg/L of influent MTBE. The Freundlich parameters are presented in Table II. The Freundlich K is related primarily to the capacity of the adsorbent, while the coefficient 1/n is a function of the strength of adsorption (18).

Both Figure 3 and Table II show the PCB GAC to have higher equilibrium adsorption capacity than the CC-602 GAC in all the water sources investigated. In addition, Figure 3 and Table II also show the magnitude of reduction in equilibrium adsorption capacity of the GAC for MTBE due to competitive adsorption of NOM present in the natural water sources (as characterized by the TOC concentration and SUVA), with higher reductions resulting from higher NOM of the water sources.
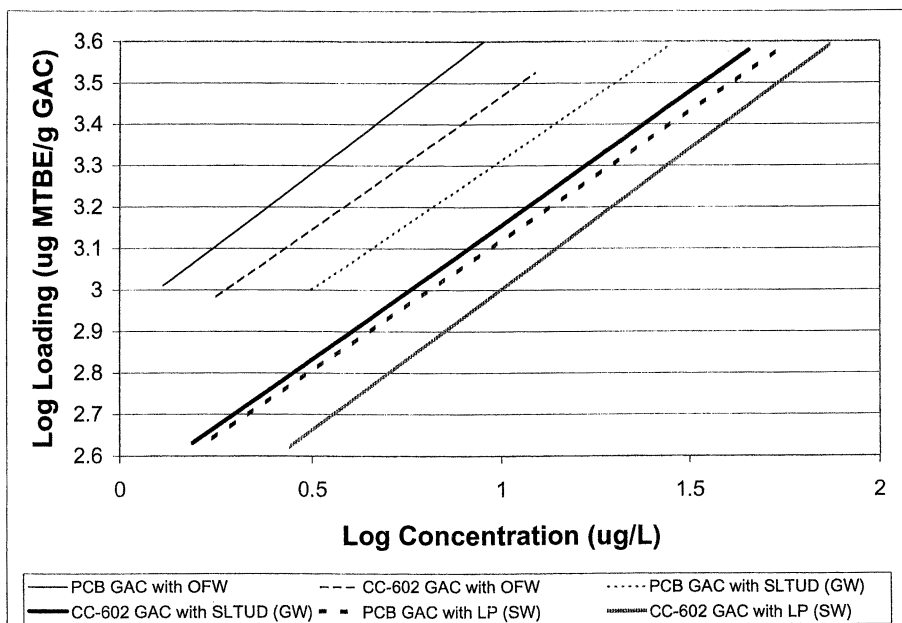
Figure 3. Isotherm of two coconut GACs in organic-free water and in three natural waters. Best fit line is shown for clarity. Actual data points are not shown (Data from reference 26).

Table II. Freundlich Parameters for PCB and CC-602 GAC in Various Water Sources

Water Source	Coconut GAC	Freundlich Constant K $(\mu g/g)(L/\mu g)^{1/n}$	Freundlich Coefficient $1/n$
Organic-Free Water	PCB	853.89	0.700
	CC-602	665.27	0.645
South Lake Tahoe Utility	PCB	489.22	0.623
District (Groundwater)	CC-602	323.52	0.645
Arcadia Well Field, Santa	PCB	416.39	0.623
Monica, CA (Groundwater)	CC-602	251.88	0.684
Lake Perris	PCB	308.60	0.629
(Surface Water)	CC-602	207.87	0.682

SOURCE: Data are from Reference 26

Cost Analysis for Adsorption as the Sole Process in MTBE Removal

Cost analysis was performed using information on unit adsorbent costs provided by the manufacturers and carbon usage rates (CUR) derived from the isotherms. Three simplifying assumptions were made: 1) the adsorbents can not be regenerated; 2) the capital costs (such as construction cost) were neglected; and 3) no additional costs were associated with the replacement of adsorbents.

Table III. Estimated Capital Costs for Some Representative System Configurations and Influent MTBE Concentrations

Flow Rate (gpm)	System Configuration	Influent MTBE (ppb)	Amortized Capital ($)[a]	Annual Capital Cost ($) per 1,000 gal
60	Two 2,500 lb vessels in series	20	6,012	0.19
60	Three 5,000 lb vessels in series	200	13,923	0.44
600	Two parallel sys. w/ two 20,000 lb vessels in series	20	43,306	0.14
600	Two parallel sys. w/ three 20,000 lb vessels in series	200	63,579	0.20

NOTE: [a] Amortization based on 20 year period at 4% discount rate
SOURCE: Data are from Reference 24

Table III shows the range of capital costs, system configurations, and MTBE influent concentrations that are representative of GAC systems treating water from contaminated drinking water sources that were not incorporated into the present cost analysis. The capital costs would include the cost of the carbon adsorption unit, piping/valves/electrical, site work, contractor overhead and profit, engineering, and contingency (*24*).

Table IV. Cost Evaluation for Adsorption as the Sole Process for South Lake Tahoe Utility District

MTBE Levels (µg/L)	Coconut GAC	Capacity (mg/g)	Theoretical CUR (lbs/1,000 gal)	Cost Per 1,000 Gal treated ($)
20	PCB	3.16	0.053	0.066
	CC-602	2.24	0.075	0.101
100	PCB	8.60	0.097	0.121
	CC-602	6.31	0.132	0.178
1000	PCB	36.08	0.231	0.289
	CC-602	27.89	0.299	0.404
2000	PCB	55.56	0.300	0.375
	CC-602	43.62	0.383	0.517

SOURCE: Data are from Reference 26

Table V. Cost Evaluation for Adsorption as the Sole Process for Lake Perris

MTBE Levels (µg/L)	Coconut GAC	Capacity (mg/g)	Theoretical CUR (lbs/1,000 gal)	Cost Per 1,000 Gal treated ($)
20	PCB	2.03	0.082	0.103
	CC-602	1.61	0.104	0.140
100	PCB	5.58	0.150	0.188
	CC-602	4.81	0.173	0.234
1000	PCB	23.74	0.351	0.439
	CC-602	23.14	0.361	0.487

SOURCE: Data are from Reference 26

Tables IV and V present a cost evaluation for adsorption as the sole process using groundwater from SLTUD and surface water from LP, respectively. The CUR and cost data for adsorption as the sole process were derived from

isotherms conducted with 1,000 μg/L of influent MTBE in specific water sources. They show the PCB GAC to have higher capacity, lower theoretical CUR, and lower cost per thousand gallons treated as compared to the CC-602 GAC for MTBE levels ranging from 20 to 1,000 μg/L. A comparison of Tables IV and V shows that the performance of the two coconut GACs decreased as the water source used changed from low TOC (SLTUD) to medium TOC (LP) content, demonstrating the competitive effect due to NOM. For instance, at the MTBE influent concentration of 100 μg/L, the CUR and cost per 1,000 gallon treated for the PCB GAC in LP water is approximately 1.5 times greater than in SLTUD water.

Cost Analysis for Adsorption as polishing Process after Application of AOP

Table VI presents a cost evaluation of adsorption as the polishing process after AOPs for GRC-22 coconut GAC conducted in groundwater from Santa Monica, CA (with TOC = 0.5 mg/L). The CUR and cost data for adsorption as the polishing process were derived from isotherms conducted with 100 μg/L of TBA in addition to 1,000 μg/L of influent MTBE. The results show the addition of TBA caused a significant decrease in GAC performance and a corresponding increase in CUR and cost. At 100 μg/L of influent MTBE concentration, the cost per 1,000 gallon treated with the addition of TBA increased to almost two fold of the cost without TBA.

Table VI. Cost Evaluation for Adsorption as Polishing Process after Advanced Oxidation Processes

MTBE Level (μg/L)	With TBA	Without TBA	Theoretical CUR (lbs/1,000 gal)	Cost Per 1,000 Gal Treated ($)
20	X^a		0.25	0.31
20		X	0.20	0.25
100	X^a		0.39	0.49
100		X	0.20	0.25
1000	X^a		0.75	0.94
1000		X	0.20	0.25

NOTE: X^a = tert-butyl alcohol at 100 μg/L
SOURCE: Data are from Reference 7

Isotherm Vs. Rapid Small-Scaled Column Tests

Isotherms obtained in this evaluation yield useful information on both the differences between adsorbents and the magnitude of competitive effects. Because equilibrium adsorption capacity for an adsorbent is a major determinant of the adsorbent's performance in columns, the isotherm can be used to compare and to screen candidate adsorbents (18), as was shown above. However, since an isotherm is a static, equilibrium test, several limitations affect the extension of isotherm data to estimate other GAC column operational or kinetic parameters (19). The RSSCT procedures developed by Crittenden et al. (20, 21, 22) used dimensional analysis or mathematical models to elucidate the relationship between the breakthrough curves of full-scale and small-scale columns. The breakthrough curve is a plot of the column effluent concentration as a function of either the volume treated, the time of treatment, or the number of bed volumes treated (18). The RSSCTs have shown (19, 20, 21, 22, 23) to yield small-scale column breakthrough curves that are equivalent to those of a full- or pilot-scale breakthrough curves in a much shorter time period, thus allowing for the optimization of design or operational parameters such as GAC type, empty bed contact time (EBCT), and operational time (e.g. number of bed volumes or operational days).

RSSCT Results on the Impact of NOM on GAC Adsorption

Studies have shown the presence of NOM can cause significant reduction in the adsorption capacity of GACs for target organics (18, 24, 27, 28, 29, 30). NOM can impact the adsorption of trace organics to GACs in three ways: 1) NOM can reduce the number of adsorption sites available to target organics either by competition for sites or by pore blockage (18); 2) NOM maybe more strongly adsorbed to the GAC, causing competitive displacement of trace organic compounds (31); and 3) Irreversible adsorption by NOM to GAC adsorption sites may permanently remove those sites from adsorption to trace organics (31).

Figure 4 is a comparison of the breakthrough curves generated through RSSCTs for PCB GAC in the three drinking water sources investigated (26). The RSSCTs were conducted with MTBE concentration of 20 µg/L, which is representative of contaminated drinking water sources. Stainless steel columns (0.5 cm diameter and 15 cm in length) with 100-mesh stainless steel screens and Teflon endcaps were used. The RSSCTs of 60 × 80-mesh size were designed to simulate pilot or full-scale columns that had an EBCT of 10 or 20 min. It shows the performance of the PCB GAC (e.g. liters of water treated per gram of PCB GAC) increased as the water in which the RSSCT was conducted changed from LP to ARWF to SLTUD. The reduction in GAC performance is most striking
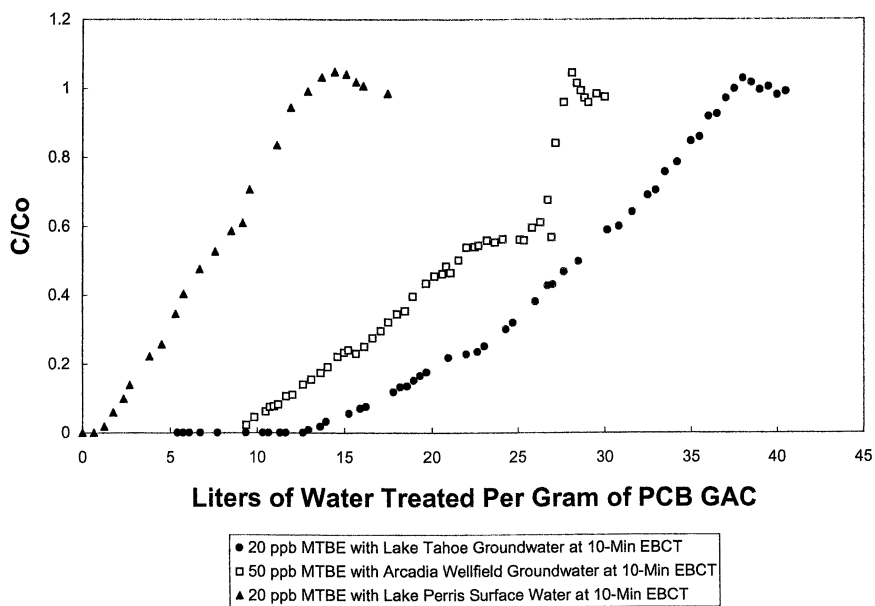
Figure 4. A comparison of the breakthrough curves for the PCB GAC in three natural water sources (Data from reference 26).

when the breakthrough curves for SLTUD and LP were compared. At 50% breakthrough, the PCB GAC was able to treat 28.2 compared to 7.4 liters of water per gram using water from SLTUD rather than from LP, an almost four-fold change in volume. This result is consistent with the TOC content of the two waters which ranges from 0.2 mg/L (low) to 3.2 mg/L (medium) for SLTUD and LP, respectively, and shows that the NOM present in the waters significantly affected the performance of the GAC columns. For the present study, the measured TOC content serves as a good indicator of the GAC fouling potential. It should be noted that the reduction in GAC performance for ARWF would clearly have been less if the influent concentration with which the RSSCT was conducted was 20 instead of the 50 µg/L that was actually used.

Comparison of Isotherm with RSSCT Results

The combination of pure isotherms and isotherms conducted using site-specific water (e.g. competitive isotherms) yield important information regarding both the equilibrium capacity of different GACs and the magnitude of the competitive effect arising from NOM and competing chemical species. The static nature of the isotherm tests limits the extension of its predictive capability to full-scale operational parameters. In addition, the equilibrium adsorption capacity data generated by isotherms are basically maximum adsorption capacities that may be much higher than what the actual GAC column operations could obtain. Comparison of pure and competitive isotherm data with data generated from RSSCTs would serve to validate the results of RSSCTs and to estimate the magnitude of the additional reduction in GAC capacity when dynamic rather than equilibrium testing are performed.

Table VII presents the data derived from RSSCTs conducted at 10 minute empty bed contact time (EBCT) in the three natural water sources. Comparing Tables IV, V, and VII, it is clear that the GAC performance as derived from RSSCT studies is much reduced compared to results obtained through the application of isotherms. The GAC capacity of the RSSCTs ranged from ~ 7 to ~ 32 percent of the capacity derived through isotherms, with greater discrepancy between the two tests associated with lower influent concentrations and/or higher TOC or NOM content of the water sources used. In fact, the CURs derived from RSSCTs with PCB GAC conducted in LP, a surface water with higher TOC or NOM content than groundwater from SLTUD or ARWF, are over 7 times the CURs derived from isotherm testing.

Table VII. Rapid Small-Scale Column Tests Data at 10 Minute EBCT

Water Source	Carbon	MTBE Influent Conc. (μg/L)	GAC Capacity at Saturation (mg/g)	CUR at Saturation (lbs/1,000 gal)
SLTUD	PCB	20	0.55	0.222
(Groundwater)	CC-602	1964	13.53	0.704
ARWF	PCB	220	3.63	0.348
(Groundwater)				
LP	PCB	20	0.14	0.611
(SurfaceWater)	CC-602	20	0.11	0.627

SOURCE: Data are from Reference 26

A number of possible factors may contribute to cause such a discrepancy between the data derived from RSSCTs and isotherms. The equilibrium adsorption capacities generated by isotherms are basically maximum adsorption capacities that may be much greater than what the actual GAC column operations or what dynamic testing such as RSSCT could obtain. The competitive effects of NOM on MTBE adsorption are usually much greater than in actual columns since all the activated carbon in a batch isotherm test is in equilibrium with the influent compound of interest and are exposed equally to all fractions of NOM present in the natural water (18, 30). In contrast, different fractions of NOM will separate in a column in accordance to their adsorption strength and affinity, leading to selective accumulation along the length of the column, with the upper and lower reaches of the column dominated by strong and weak adsorbing NOM fractions, respectively (18, 30). The greater discrepancies between RSSCTs and isotherms observed as the TOC or NOM content of the water source used were increased maybe explained by the increased competitive adsorption or NOM fouling of the RSSCTs compared to the competitive isotherms at higher NOM concentrations.

Comparatively, the RSSCTs are a more sophisticated and time consuming testing procedure than the isotherms. A large number of GACs and other adsorbents under a variety of conditions (e.g. different water sources, different competitive adsorbate composition and concentrations) maybe tested simultaneous through the isotherm testing procedure. However, it is by definition a static test that yields adsorption capacity under equilibrium conditions. Consequently, the isotherm tests maybe used as a preliminary screening tool for comparing the relative effectiveness of different adsorbents and the magnitude of competitive effects arising from competing chemical species. The specific or operational adsorption capacities may then be derived

from the performance of RSSCTs using the most promising adsorbents selected from the isotherm tests.

Summary

Adsorption is a viable and important process in the removal of organic compounds from water. The physical and chemical characteristics of MTBE cause the compound to preferentially remain in solution, rendering most traditional treatment technologies ineffective. Careful evaluation is thus needed to define the optimum conditions under which the adsorption process would be cost effective.

Pilot columns have been shown to be accurate and reliable predictors of breakthrough behavior in full-scale columns in terms of both capacity and kinetics of adsorption. However, pilot columns have equivalent operation time as full-scale systems, coupled with the high capital investments required for the pilot system and the necessity to screen all types of adsorbents, it becomes clear that the operation of pilot columns as a screening and optimization tool is not feasible. Isotherms and RSSCTs are two bench-scale tests that have been shown to be accurate and reliable predictor of breakthrough behavior of full-scale adsorber systems. This study demonstrates through the application of isotherms and RSSCTs that the coconut GAC is the most cost-effective adsorbent. In addition, the impact of NOM on GAC performance was found to be significant, with the measured TOC content of the waters serving as a good indicator of the GAC fouling potential.

Future research should concentrate on investigating promising adsorbents identified in this or other studies through screening processes such as the isotherms. The adsorption properties of the adsorbents may then be quantified by more site-specific dynamic column testing such as the RSSCTs.

Acknowledgments

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Chapter 16

Biodegradability of Methyl *tert*-Butyl Ether and *tert*-Butyl Alchohol

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Uncertainty regarding a continued reliance on biological processes for remediation at gasoline-contaminated sites has increased over the past several years due to the addition of methyl *tert*-butyl ether (MTBE) to gasoline and its subsequent discovery in groundwater. Contrary to early reports of MTBE and TBA (*tert*-butyl alcohol) recalcitrance, a review of the recent literature and of on-going studies suggests that both compounds are degradable by a wide range of microorganisms. The objectives of this manuscript are to provide a brief review of laboratory and field studies addressing MTBE and TBA biodegradation, and to evaluate the current understanding of the factors that could limit their bioattenuation in the environment.

The production and addition of methyl *tert*-butyl ether (MTBE) to gasoline increased significantly during the last decade as a result of the Clean Air Act Amendments of 1990 which mandated the use of reformulated gasoline and oxygenated fuel in ozone and carbon monoxide non-attainment areas, respectively. MTBE can be accidentally introduced to subsurface environments during the refining, distribution and storage of oxygenated fuels. Due to its unique physical and chemical properties, MTBE has been shown to migrate in subsurface environments with minimal retardation relative to other gasoline components. The occurrence of MTBE in drinking water supply wells has

increased over the past several years resulting in significant national concern about the continued use of MTBE in gasoline (*1*). As a result, the biodegradability of MTBE has received considerable attention lately and the bioremediation of MTBE-impacted groundwater has become an increasingly active area of basic and applied research.

As the problems associated with MTBE contamination continue to emerge and magnify, so does interest in the fate and transport of *tert*-butyl alcohol (TBA) in subsurface environments. TBA can be present as an impurity in MTBE-blended gasoline. In addition, microbial oxidation and hydrolysis of MTBE in aquatic environments has been shown to produce TBA.

The overall objective of this chapter is to provide a brief summary of laboratory and field studies addressing the degradation of both MTBE and TBA. In addition, key variables that significantly influence the biodegradation of MTBE in the environment will be discussed with a focus on those potentially responsible for optimizing biodegradation processes in both *in situ* and *ex situ* applications.

Review of MTBE and TBA Biodegradation Studies

Alkyl ethers, such as MTBE, are relatively difficult to degrade due to the high energy required by microorganisms to cleave the ether bond and the resistance of the branched carbon structure to microbial attack (*2-4*). Several studies initially reported that MTBE is biologically recalcitrant under most environmental conditions (*5-8*). Recent laboratory and field studies, however, have reported the ability of a number of bacterial and fungal cultures from various environmental sources to degrade MTBE under aerobic and anaerobic conditions, either as a sole source of carbon and energy or cometabolically. A review of these studies is presented below.

Aerobic Degradation

Both laboratory and field studies have reported the biodegradation of MTBE and TBA under aerobic conditions. A detailed review of these studies is available elsewhere (*9*). A summary of representative laboratory studies is presented in Table I. In these studies, MTBE and TBA were either metabolized as primary substrates, or were degraded cometabolically by cultures grown on alkanes or aromatic compounds (*2, 10-24*). MTBE degradation was shown to occur in the presence of oxygen with half-lives ranging from 0.04 to 29 days. Reported degradation rates ranged from 0.3 to 50 mg MTBE/g cells/h. Growth rates on MTBE were also low, ranging from 0.01 to 0.04 g MTBE/g cells/d. In

Table I. MTBE and TBA Degradation Rates from Representative Laboratory Studies

Culture	MTBE Degradation Rate	TBA Degradation Rate	Reference
Mixed (MTBE-grown)	34 mg/g cells/h	14 mg/g cells/h	10
Mixed (MTBE-grown)	MTBE > TBA [a]	TBA < MTBE [a]	11-12
Mixed (MTBE-grown)	1.1 - 2.6 mg/L/h [b]	1.8 - 2.8 mg/L/h [b]	13
Pure (MTBE-grown)	1.9 mg/L/h [c] 50 mg/g cells/h	2.2 mg/L/h [c] Not measured	14-16 54
Pure (MTBE-grown)	0.18 mg/L/h [d]	Not degraded	2
Pure (cometabolic)	17 - 44 mg/g cells/h [e]	9.0 mg/g cells/h [e]	17
Pure (cometabolic)	6.1 - 27 mg/g cells/h [e]	3.8 - 7.0 mg/g cells/h [e]	18
Pure (cometabolic)	11 mg/g cells/h [e]	2.8 mg/g cells/h [e]	19
Pure (cometabolic)	Not degraded	18 mg/g cells/h [e]	20
Pure (cometabolic)	0.92 mg/g cells/h	Not degraded	21
Microcosm (sediments)	30 - 70% mineralized in 2520 h	70% mineralized in 648 h	22
Microcosm (groundwater)	Not degraded	Half-life = 384 h	23
Microcosm (soil)	Not degraded	6.3×10^{-4} mg/L/h	24

[a] Rate not reported
[b] Cell inoculation density not reported
[c] Cell inoculation density not measured
[d] Cell inoculation density = 5×10^5 - 5×10^7 CFU/mL
[e] Literature values reported in nmol/min/mg protein. Values calculated in mg MTBE/g cells/h assuming the following: 0.55 g protein/g cells.

addition, reported cellular yields with MTBE were generally much lower than those with other gasoline constituents. As a result, it has been suggested that MTBE may behave as a metabolic or electron transport inhibitor or as an uncoupler of ATP formation (*10*).

A number of microcosm studies have reported the biodegradation of MTBE in soil and groundwater samples obtained from gasoline-impacted sites. For example, high concentrations of MTBE were degraded in groundwater samples from a gasoline-contaminated aquifer in Nevada at rates of 0.01 to 0.32 mg MTBE/g cells/d (*23*). In soil and groundwater samples from a site in New Jersey, MTBE was degraded at a rate of 0.28 mg/L/d with a half-life of 21 days (*23*). While in some instances MTBE and TBA were degraded in other soil and groundwater microcosms (*22, 25-28*), the evidence to date suggests that the bioattenuation of MTBE in subsurface environments is mostly a function of site specific conditions. A survey conducted to evaluate the presence of naturally-occurring MTBE-degraders at 10 gasoline-contaminated sites located throughout the United States indicated that populations of MTBE-degrading microorganisms were typically low in subsurface environments with concentrations below 10^3/g soil or 100/L groundwater as measured using the most probable number serial dilution method (*23*).

The degradation of MTBE under aerobic conditions has also been demonstrated in laboratory and pilot scale fixed-film and suspended-growth bioreactors. Fixed-film bioreactors are capable of retaining slow-growing bacteria that might otherwise be washed out from suspended-growth reactors. Given the low cellular yields of MTBE-degraders, fixed-film bioreactors can be effective in enriching and retaining MTBE-degrading cultures. In fact, results from biotrickling filter studies at UC Riverside suggest that attached growth could be a key factor in obtaining and maintaining active MTBE-degrading populations in engineered reactors (*29-30*). In biofilters, MTBE removal rates ranged from 6 to 50 g MTBE/m^3 reactor volume/h (*29-32*). Results from two field studies conducted in Nevada and California with up-flow fluidized bed bioreactors containing granular activated carbon packing media used to treat hydrocarbon-contaminated groundwater suggest that high MTBE removal efficiencies can be achieved and retained over extended periods of time (*33*). In contrast to fixed-film bioreactors, suspended-growth bioreactors typically utilize concentrated suspensions of cells to degrade high concentrations of organic contaminants. The main advantage of using suspended cultures in stirred vessels is the enhanced contact of microorganisms with aqueous phase contaminants, dissolved oxygen and nutrients. Cell recycling has been shown to be an important step during the treatment of MTBE-contaminated water since it conserves the biomass of MTBE-degrading populations. For example, a membrane bioreactor was recently used to treat an MTBE-contaminated water stream in New Jersey. The microbial population in the bioreactor was shown to reduce MTBE concentrations from approximately 2,400 mg/L to as low as 1.6

mg/L, with an average removal rate of 96% over the course of the study (*34*). Bioreactors seeded with other MTBE-degrading cultures have been recently shown to degrade high concentrations of MTBE (up to 2000 mg/L) with average effluent concentrations of less than 100 µg/L (*35*).

Examples of representative field studies of various aerobic treatment approaches are presented in Table II.

Anaerobic degradation

Limited studies have evaluated the degradability of MTBE and TBA under anaerobic conditions. Yeh and Novak (*39*) evaluated the biodegradation of MTBE in soils from three different sites under various anaerobic and anoxic conditions. They reported that the biodegradation of MTBE was observed under methanogenic conditions in a soil with low organic carbon content. The co-existence of easily degraded organic compounds was shown to inhibit MTBE degradation. While there have been few successful laboratory or field experiments demonstrating MTBE biodegradation under anaerobic conditions, there is some evidence that MTBE can be degraded under methanogenic conditions (*40-41*). In addition, unpublished studies by the United States Geological Survey and the University of Massachusetts have implied that MTBE can be potentially degraded under nitrate- and iron-reducing conditions in microcosms prepared using aquifer materials from contaminated sites (*42, 43*). Finally, while MTBE concentrations have decreased at some field sites under anaerobic conditions, the mechanisms and limitations of MTBE degradation in the absence of oxygen remain unclear.

TBA degradation has also been shown to take place under anaerobic conditions in a range of soils at rates of 0.05 to 0.15 mg/d/g soil suggesting that a number of naturally-occurring TBA degraders are present in subsurface environments (*39*).

Mechanisms of MTBE and TBA Biodegradation

Although several pure and mixed cultures have been reported to degrade MTBE, the metabolic pathway has not been fully elucidated. Results from several studies suggest that under aerobic conditions, the ether bond is enzymatically cleaved yielding TBA and formaldehyde as the predominant detectable metabolic intermediates (*18*). Some studies, however, suggest that *tert*-butyl formate (TBF) could be the first metabolite of MTBE degradation (*21*) and that due to its rapid hydrolysis rate, it is quickly converted to TBA rather than accumulating to detectable levels (*44*). TBA has been shown to further

biodegrade to 2-methyl-2-hydroxy-1-propanol (MHP) and 2-hydroxyisobutyric acid (HIBA) (Figure 1). Speculated downstream intermediates of MTBE include 2-propanol, acetone and hydroxyacteone (*14-15, 18*). Most aerobic MTBE biodegradation reports suggest that a monooxygenase enzyme is involved in the initial biotransformation of MTBE to TBA (*18, 21*). A monooxygenase enzyme is also responsible for the initial attack on TBA. It is unclear, however, whether MTBE monooxygenase is also responsible for TBA degradation. Results from a number of biochemical studies suggest that the degradation mechanisms of MTBE and TBA could be culture dependent (*15, 17*). It is also unclear from previous studies whether the enzymatic attack on MTBE or TBA is the rate-limiting step for the complete degradation of MTBE. In fact, the observed range of results with respect to the accumulation of TBA during MTBE degradation suggests that the degradation kinetics for the two compounds can differ significantly among different species.

The metabolism of both MTBE and TBA in animal and human tissues has also been investigated. Results suggest that, in most cases, the intermediates of MTBE metabolism by eukaryotic cells are the same intermediates associated with its prokaryotic metabolism. For example, TBA has long been known to be the major product of MTBE metabolism in tissues of mice and rats (*45-46*).

Studies that have evaluated the metabolism of MTBE by humans also suggest that the major detectable intermediates were MPH and HIBA with traces of formaldehyde and acetone (*47*). All of these compounds are intermediates of MTBE metabolism by bacterial cells (Figure 1).

Key Factors Affecting MTBE and TBA Biodegradation in Subsurface Environments

Oxygen concentration

Most of the cultures reported to degrade MTBE in laboratory studies have been shown to require oxygen concentrations greater than 2 mg/L (*11-12, 48*). In addition, *ex situ* studies have demonstrated the dependence of MTBE degradation on adequate concentrations of molecular oxygen (*29-30, 49-50*). Several *in situ* field studies have also demonstrated the importance of oxygen in stimulating MTBE degradation (*27, 51-53*).

The observed relationship between MTBE biodegradation rates and levels of dissolved oxygen suggests that the effectiveness of engineered bioremediation systems in subsurface environments could depend upon the ability to transport and sustain adequate oxygen concentrations throughout the MTBE biodegradation zone.

Table II. Summary of Representative MTBE Biodegradation Field Studies

Treatment Type (Site Location)	Culture	Notes	Reference
Ex situ (Sparks, NV)	Fixed-film bioreactor Naturally-occurring cultures	Long start-up (400 d) HRT = 0.2 h 83% average removal for MTBE	33
Ex situ (San Diego, CA)	Fixed film bioeactor Naturally-occurring cultures Cometabolic	Short start-up (20 d) HRT = 1.4 h 95% average removal for MTBE	33
Ex situ (Envirogen, NJ)	Suspended-growth bioreactor Pure culture, ENV42 Cometabolic	Iso-propanol used as primary substrate HRT = 3.3 - 5 d 96% average removal for MTBE	34
In situ (British Petroleum, FL)	Natural attenuation Indigenous cultures	Multiple gasoline-contaminated sites from UST's at BP stations 89% of MTBE plumes decreased in size MTBE attenuation rate comparable to that of benzene	36
In situ (Ontario, Canada)	Natural attenuation Indigenous cultures	Controlled release 97% of the mass of MTBE disappeared after 8 years Half-life ~ 578 d	28

In situ (Oscoda, MI)	Natural attenuation Indigenous cultures	Controlled release TBA was formed then disappeared 10% of the MTBE in 150 ft of the plume Half-life ~ 756 d	37
In situ (Port Hueneme, CA)	Bioaugmentation Mixed culture, BC–4	Initial MTBE concentration = 2-8 mg/L Half-life ~ 693 days in control plot Half-life ~ 99 days in O_2-only plot Half-life ~ 18 days in BC-4/O_2 plot	27
In situ (Port Hueneme, CA)	Bioaugmentation Pure culture, PM1	Ongoing study MTBE degradation fastest in bioaugmented test area MTBE degradation also observed in area injected with oxygen only but lag period longer	38

MTBE

CH₃—C—O—CH₃ (with CH₃ above and CH₃ below)

→

Formaldehyde + TBA

CH₃—C—OH (with CH₃ above and CH₃ below)

→

CH₃—C—CH₂—OH (with CH₃ above and OH below)

2-methyl-2-hydroxy-1-propanol

2-propanol

CH₃—C—OH (with CH₃ above and H below)

→

HIBA

CH₃—C—C (with CH₃ above, =O; OH and OH)

→

Acetone

CH₃—C—CH₃ (with =O)

→

Hydroxyacetone

CH₃—C—CH₂—OH (with =O)

→ Pyruvic acid

Figure 1. Proposed metabolic pathway for the degradation of MTBE.

Co-occurring contaminants

MTBE is most often found at sites that are impacted by complex mixtures of gasoline hydrocarbons, some of which have been shown to promote the cometabolic biodegradation of MTBE. These compounds are most typically short-chain alkanes and their success in stimulating the cometabolic degradation of MTBE has been limited to laboratory and *ex situ* pilot demonstrations (*17-19, 21*).

Alternatively, MTBE biodegradation may be inhibited in the presence of more easily biodegradable compounds. This inhibition can occur when MTBE-degrading cultures preferentially utilize easily degradable hydrocarbons such as BTEX compounds (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene) instead of MTBE. Inhibition can also occur when preferential hydrocarbon use causes the depletion of electron acceptors and nutrients in mixed contaminant plumes, thereby limiting MTBE biodegradation. Few studies have evaluated the effect of substrate interactions on the biodegradation rates of MTBE and BTEX compounds in contaminant mixtures. In one study, the cometabolic degradation of MTBE by cultures grown on benzene or *o*-xylene was severely retarded by low concentrations of benzene (0.15 mg/L) (*52*). In another study with a pure culture, PM1, the presence of benzene and toluene significantly delayed the onset of MTBE biodegradation, while ethylbenzene and the xylenes completely inhibited biological activity (*54*). The impact of increasing concentrations of toluene on MTBE degradation was recently evaluated in a biofilter study (*31-32*). Increasing concentrations of toluene significantly decreased MTBE removal efficiency presumably due to nitrogen limitation at higher carbon loading rates. Finally, in studies by Church et al. (*26*), the biodegradation of MTBE was evaluated in laboratory columns packed with aquifer material from 4 different sites. MTBE was shown to degrade but only in the absence of BTEX compounds. Controlled field studies are needed to elucidate MTBE degradation potential in mixed contaminant plumes.

In Situ Bioremediation Approaches at MTBE-Impacted Sites

Biological removal of MTBE has yet to be widely applied in the field. Several studies have suggested that in some cases, intrinsic *in situ* bioremediation was responsible for MTBE mass losses in contaminated aquifers (*25, 28, 36*). However, conclusive evidence supporting such observations was not found. Engineered *in situ* bioremediation involves the stimulation of microorganisms within a subsurface aquifer to degrade contaminants of concern by active manipulation of existing physical, chemical or biological conditions. In most cases, stimulation of microbial populations requires the addition of

electron acceptors, inorganic nutrients, or a primary substrate if the contaminant of concern is not a good source of carbon and energy (55). In some cases, the addition of exogenous microorganisms, or bioaugmentation, can be used to promote contaminant destruction.

Biostimulation generally relies on naturally-occurring microorganisms to degrade organic compounds with the support of introduced electron acceptors, nutrients and co-substrates. Biostimulation with oxygen addition has been successfully performed at MTBE-contaminated sites using air sparging, oxygen sparging or oxygen release compounds (27, 37, 51-53). Biostimulation can also include the addition of a primary substrate to effect the cometabolic biodegradation of MTBE. Potentially successful cometabolites for MTBE degradation include *iso*-propanol, propane and *n*-butane. Researchers at Envirogen are proposing propane injection into subsurface environments to stimulate MTBE biodegradation by naturally-occurring propane-oxidizing bacteria (35).

Bioaugmentation is being implemented at several MTBE-contaminated sites. Pure and mixed microbial cultures with the ability to effectively degrade MTBE are being utilized (10, 16, 18). Slurries of MTBE-metabolizing mixed and pure cultures have been recently injected in test areas at Port Hueneme, California (27, 38). In both cases, the remedial systems were designed such that the plume migrated through a microbial barrier. Results from the two studies revealed that bioaugmentation with oxygen injection was more effective than oxygen injection alone in promoting the biodegradation of MTBE in the aquifer. Furthermore, a shorter lag period for the degradation of MTBE was observed when bioaugmentation was used (27). These studies suggest that bioaugmentation combined with oxygen amendment appears to be a feasible *in situ* MTBE treatment option. Finally, researchers at Envirogen have recently injected a slurry of a propane-oxidizing pure culture, ENV425, together with dissolved propane at a gasoline-contaminated site in New Jersey to effect *in situ* MTBE biodegradation (35).

Conclusions

A range of microbial cultures from diverse environments can efficiently degrade both MTBE and TBA. The successful removal of MTBE from contaminated fluids has been demonstrated in a number of pilot and field scale fixed-film and suspended-growth bioreactors. While in some instances MTBE was shown to degrade in laboratory aquifer microcosms and at gasoline-contaminated sites, there are no compelling indications to date that the bioattenuation of MTBE is occurring naturally at appreciable rates in subsurface environments. Conclusive information on the natural attenuation potential of

MTBE is needed prior to its acceptance by the regulatory community as a control strategy for MTBE remediation. However, engineered bioremediation for enhanced MTBE removal by means of oxygen addition, co-substrate addition, and/or bioaugmentation has shown promising results in a number of field trials.

Even though the results of the reviewed reports vary to some extent, several conclusions can be made regarding the biodegradation potential of MTBE and TBA by microbial populations:

1. MTBE and TBA have the potential to be biodegraded under aerobic conditions either as sole carbon and energy sources, or cometabolically with alkanes or aromatic compounds.
2. The cellular yield of microorganisms utilizing MTBE or TBA as the sole carbon source appears to be low.
3. The presence of more easily biodegradable organic compounds in the subsurface can either inhibit MTBE or TBA biodegradation, or in limited cases, possibly promote their cometabolic degradation.
4. While MTBE and TBA have been shown to degrade under anaerobic conditions, the most rapid biodegradation rates have been reported aerobically. Furthermore, neither mixed nor pure cultures with the ability to mineralize MTBE in the absence of oxygen have yet been identified. As a result, the mechanisms of anaerobic MTBE degradation remain relatively unknown.
5. Based on a review of several case studies, it appears that MTBE bioremediation strategies including bioenhancement (addition of oxygen, nutrients or co-substrates), bioaugmentation, or a combination of both, have a strong potential for success.

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Chapter 17

Applying Co-Metabolic Biological Reactions for the Ex-Situ Treatment of Methyl *tert*-Butyl Ether Contaminated Groundwater

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Abstract

Methyl *tert*-butyl ether (MTBE) has become a widespread ground water contaminant in the United States. The rapidly increasing impact on public drinking water supplies has created an urgent need to develop an economical treatment technology that can treat large volumes of water to low MTBE concentrations. Prior research has shown that MTBE can be degraded by bacteria either as a carbon and energy source or co-metabolically. In this paper, fluidized-bed bioreactors treating MTBE contaminated ground water were examined to determine the mechanism (growth based or co-metabolic) by which MTBE was biodegraded. It was determined that the predominant mechanism was a co-metabolic degradation process. Further investigation revealed that fatty acids (lactate and acetate) and alkanes (*iso*-pentane) could serve as co-metabolites for stimulating MTBE biodegradation. Field and laboratory testing indicates that *iso*-pentane is the superior co-metabolite for stimulating MTBE removal, because of it's selectivity for MTBE degraders.

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Introduction

Approximately 70% of all gasoline in the United States contains methyl *tert*-butyl ether (MTBE) and, as a consequence, MTBE has become a widespread ground water contaminant (*1, 2, 3, 4*). Only selected individual compounds such as *iso*-pentane (*ca.* 12%) toluene (*ca.* 8%), 2-methyl pentane (ca. 5%), m-xylene (*ca.* 4 %) and *n*-pentane (*ca.* 3%) approach the concentrations of MTBE (15 %) found in reformulated gasoline. Unlike the natural components of gasoline, MTBE can migrate long distances in ground water (*1, 4*).

Ground water contamination problems are especially of concern in California and other Western states where oxygenated fuels are used extensively and the population relies heavily on ground water for their drinking water. California is responsible for 25% of the global MTBE consumption, which is largely utilized in gasoline (*5*). A survey published in 1998 demonstrated that MTBE contamination is now found at the majority of leaking underground fuel tank sites in California (*1*). MTBE has been detected in municipal drinking water supplies throughout California and in some cases supply wells have been closed due to high levels of MTBE contamination (*1, 4*). MTBE contamination of ground and surface water has created a political up-roar in California (*6*). The level of contamination is considered of great enough concern that the Governor of California has issued an executive order restricting the use of MTBE in gasoline. MTBE use is to be completely banned in California by the end of 2002 (*7*). However, even if MTBE was eliminated from gasoline immediately, there will remain many sites in California alone that will potentially require *in-situ* or *ex-situ* remediation (*1*).

Biological treatment of MTBE contaminated ground water has only recently been considered as a potentially applicable technology. Several investigators have been able to maintain MTBE biodegrading treatment systems in the laboratory (*8, 9, 10, 11*). These laboratory reactors are typically fed MTBE as the primary or sole carbon source. In all cases the reactors exhibited slow biomass accumulation, were difficult to start, and are generally unstable, being easily subject to a loss of MTBE treatment efficiency. Similar problems have been found to plague reactors used in the field.

The most complete study available on the biological treatment of MTBE in a complex waste stream is a study in which use of a suspended growth reactor was compared to a fixed-film reactor for the treatment of tank-water spiked with MTBE (*12*). Suspended growth reactors could be used for MTBE removal, but it was concluded that fixed-film reactors were more efficient at retaining the slow growing MTBE degrading population (*12*). Due to the slow growth and low yield of MTBE degraders, it is generally agreed that fixed-film systems, such as fluidized-bed reactors, should be more practical for MTBE treatment in the field.

Full-scale biological treatment of MTBE contaminated ground water has been reported (*13, 14, 15*). Two parallel fluidized-bed reactors with a combined design capacity of 540 gpm were installed at a fuel transfer terminal in Nevada to remove benzene, toluene, ethyl-benzene, and xylenes (BTEX compounds) from gasoline contaminated ground water. The reactors began to remove MTBE after approximately 200 days of operation (*15, 14*). It was demonstrated that MTBE removal was the result of a combination of physical sorption and biodegradation, but that biological removal rates could account for the majority of MTBE treatment in the system (*16*). The system in Nevada has been treating MTBE contaminated groundwater for almost four years (*13, 14*).

Bacterial cultures capable of degrading MTBE have been described only in the last few years. Salanitro *et al.* (*11*) reported that they were able to maintain an MTBE degrading culture in a suspended growth reactor. These bacteria were shown to grow on MTBE as a sole carbon source, exhibited a slow growth rate (<0.01 day^{-1}), and were able to oxidize MTBE to CO_2 with the transitory production of *tert*-butyl alcohol (TBA) as a measurable intermediate. Bacteria capable of growth on MTBE as a sole carbon source have now been grown in a number of laboratories (*9, 8, 17*).

All cultures that grow on MTBE are characterized by slow growth rates and low cell yields (*8, 11, 17*). These characteristics are not optimal for the development of full-scale biological systems treating low influent concentrations and high flows, as is needed in most ground water treatment systems. There is also very little information available concerning how bacteria capable of growing on MTBE as a sole carbon source will respond in systems receiving other compounds in addition to MTBE. MTBE contaminated ground water may also be contaminated with gasoline, alcohols, and other more easily degraded carbon sources, as well as potentially toxic substances such as chlorinated solvents. Even in fixed film systems, slow growing organisms must compete with faster growing organisms, such as toluene degraders, for nutrients, oxygen, and space. Slow growing organisms will also be more susceptible to wash-out, as influences such as shear forces and iron deposition limit biofilm growth, attachment, and cell retention time. This competition may partially explain why MTBE degrading bioreactors are difficult to maintain in the field.

It is now well established that enzymes found in many microorganisms can act upon a broad range of substrates, in a non-specific manner not typically found in higher organisms. If the substrate transformed by the enzyme does not become a useful product that can serve as an resource for the organism and promote growth, the transformation is termed "co-metabolic." Classic examples of co-metabolic transformations that are useful in *in-situ* and *ex-situ* biological treatment include trichloroethylene transformations by toluene degraders and the transformation of benzo[a]pyrene and other high molecular weight polynuclear aromatic hydrocarbons by phenanthrene degraders (*18, 19, 20*).

It has been determined that MTBE can be degraded by microorganisms co-metabolically. Steffan *et al.* (*21*) reported that MTBE could be degraded by camphor degraders and propane oxidizing bacteria that could not use MTBE as a growth substrate. Propane oxidizers were considered the most efficient MTBE degraders and were found to metabolize MTBE to TBA and other intermediates. Hardison *et al.* (*22*) demonstrated that diethyl ether degrading fungi could also co-metabolize MTBE.

It has been shown that MTBE co-metabolism is a common characteristic of alkane degrading bacteria (*23, 24, 25*). Bacteria able to grow on *iso*-butane and *iso*-pentane, as well as propane and *n*-pentane, are active for MTBE degradation. There is evidence that MTBE is oxidized by the same oxygenase enzymes that are expressed by microorganisms to initiate growth-related oxidation of alkanes (*21, 23, 24, 25*). During the oxidation of MTBE, there is the production of an initial stable oxidation product, TBA. As is found with organisms that grow on MTBE, TBA is a transitory intermediate that is further degraded with time.

The objective of the research presented here was to determine the mechanism by which MTBE was being degraded in full-scale fluidized bed bioreactors treating MTBE contaminated ground water. Once the mechanism was determined, field and laboratory tests were conducted to evaluate improved techniques for MTBE biological treatment.

Methods

Biological reactors included in this study are up-flow, fluidized bed reactors which use granular activated carbon (GAC) for their bed material. The reactor at the California site (approximately 2,000 L) and the laboratory reactors (approximately 4 L) are essentially identical to the reactors used by Tang and Sun (*12*). At the Nevada site, there are two full-scale (10,000 L) reactors operating in parallel. Both the laboratory and field reactors are manufactured by Envirex/U. S. Filter (Waukesha, WI).

Bioreactors at both field sites receive MTBE contaminated ground water without pretreatment (*14, 13*). No additional MTBE is added to the reactors, but the ground water is supplemented with nitrogen and phosphorous to stimulate biological treatment. Laboratory bioreactors receive a synthetic feed containing gasoline and MTBE, supplemented with inorganic nutrients.

Samples of biologically active materials (GAC and floc) were collected from the fluidized-bed bioreactors located at the two field sites and shipped overnight on ice to the laboratory. These materials were used in MTBE up-take experiments and as inoculum for enrichment cultures.

Enrichment cultures were selected by inoculating field samples into Erlenmeyer flasks containing mineral salts media and the compound of interest.

Mineral salts medium was made by combining 1 g KH_2PO_4, 0.86 g Na_2HPO_4, 1 g NH_4Cl, 0.06 g $MgSO_4$, 0.06 g $CaCl_2\text{-}2H_2O$ and 1 mL trace metal solution in 1 liter of distilled-deionized water. Trace metals solution was made by combining 3.3 mg $MnSO_4\text{-}H_2O$, 6.2 mg $CuSO_4\text{-}5H_2O$, 7.6 mg $ZnSO_4\text{-}7H_2O$, 11.7 mg $Na_2MoO_4\text{-}2H_2O$, and 64.6 mg $FeSO_4\text{-}7H_2O$ in 1 liter of 0.05 N HCl.

MTBE enrichments were made at high MTBE concentrations, where MTBE was added as a vapor in constant excess, and at low concentrations where MTBE was added at less than 10 mg/L. MTBE degrading organisms were isolated on mineral media agar in an MTBE atmosphere and purified on R2A agar in a MTBE atmosphere. Culture purity was also confirmed on R2A agar without MTBE. Cultures were identified using FAME analysis (MIDI Inc., Newark, DE).

MTBE up-take experiments were conducted by combining 1.5 grams of bed material (either floc or GAC), mineral salts media, and MTBE in a 40 mL vial fitted with a Mininert™ valve. MTBE removal over time was measured by headspace analysis using GC/FID. Activity measurements on MTBE degrading cultures were conducted in a similar manner.

Results and Discussion

The original hypothesis of this project was that organisms able to grow on MTBE as a sole carbon and energy source were responsible for MTBE treatment in fluidized-bed bioreactors. The major piece of evidence supporting this argument was the extended period of time (over 200 days) it took for MTBE removal to begin in the reactor at the Nevada site (15, 14).

Enrichment cultures were started using MTBE as a sole carbon and energy source. After an extended period, some of the enrichments at high MTBE concentrations became slightly cloudy and others developed a waxy culture of bacteria at the air-water interface (dubbed "White-top"). These enrichments were plated on mineral salts agar in an MTBE atmosphere for isolation. It was found that many organisms from these enrichments were able to grow in trace organic compounds in the agar, and it was necessary to further screen the isolated organisms for MTBE removal in an MTBE up-take experiment. In the up-take experiments, it was found that several organisms exhibited growth (an increase in turbidity) without demonstrating significant MTBE degradation. Three strains of bacteria and a fungus were found to be able to degrade MTBE in liquid culture (Table 1). Two of the isolates (strains 18a and 35) were identified as *Nocardioides luteus* and *Rhodococcus erythropolis*. The "White-top" strain and the fungus could not be identified by FAME or Biolog™ analysis, however "White-top" was clearly another nocardioform.

Table 1: Screening of isolated cultures for the ability to degrade MTBE in liquid media. Percent removals in bold were significantly greater than controls.

Culture	Turbidity	% Removal
White-top	+++	**51.2**
18a	+++	**17.9**
Fungus	++	**12.5**
35	++	**11.3**
41	+	5.2
23	++	5.0
27	++	4.9
40	++	4.8
37	++	4.3
11	+	4.1
1	++	3.7
22	+	2.7
7	+++	2.1
28	+	1.3
30	+++	0.4
3a	++	-0.1
31	++	-1.2
29	+	-3.7
45	+	-4.4

The growth of bacteria on MTBE was poor. In a typical incubation, the organisms exhibited no growth or MTBE degradation for over a week and then would begin to degrade MTBE over an extended period that could last an additional 20 days or more (Figure 1). In many cases, MTBE enrichments would not maintain MTBE degrading activity after multiple transfers. Growth on MTBE gave extremely low yields of bacterial biomass. These results were consistent with results obtained by Salanitro (11, 26).

The poor growth, low activity, and instability of the MTBE degrading cultures raised several issues concerning the relative importance of growth based transformation processes in MTBE degrading fluidized-bed bioreactors. It was also apparent that trying to develop novel process control strategies for MTBE treatment would be difficult if the treatment were solely dependent on growth based processes.

It was concluded that organisms able to grow on MTBE as a sole carbon source did exist in the Nevada bioreactors, but it seemed unlikely that a growth based mechanism could account for all of the activity observed in the field. An alternative hypothesis, that co-metabolic MTBE degradation was the predominate mechanism for MTBE treatment in the Nevada bioreactors, was formulated and tested.
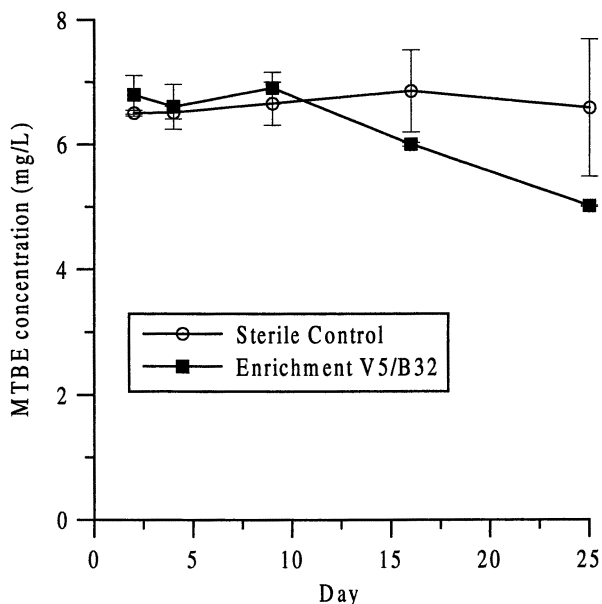
Figure 1: Degradation of MTBE by an MTBE enrichment culture. Mean plotted with error bars of one standard deviation

Ground water being treated by bioreactors at the field sites in this study is characterized by a diverse organic carbon content. In addition to MTBE, the ground water can contain benzene, toluene, ethyl-benzene, xylenes, and other petroleum hydrocarbons such as alkanes (*14, 13*). At the sites included in these studies, there are sufficient alternative carbon and energy sources to support the co-metabolism of MTBE.

A kinetic evaluation was made of samples taken from fluidized-bed reactors exhibiting good MTBE treatment efficiency (Figure 2). Fitting the Michaelis-Menten kinetic model to the data reveals that the K_m for MTBE degradation was approximately 60 mg/L. This number is surprisingly high and is much more consistent with a co-metabolic mechanism than a growth base mechanism.

Further evidence that a co-metabolic mechanism is the dominant mechanism for MTBE removal in the field reactors was obtained by directly testing samples of bed material for their ability to maintain MTBE degrading activity when repeatedly supplemented with MTBE. In one experiment, MTBE was added to bed material in a standard batch degradation assay and MTBE degradation was monitored over time. When MTBE concentration went below 0.1 mg/L, the vial was re-aerated, more MTBE was added to the culture, and MTBE removal was again followed. Results from this experiment are presented in Figure 3. As one can see, the MTBE biodegradation potential of this culture declined over time as the culture was re-supplied with MTBE. The data indicate that MTBE is not
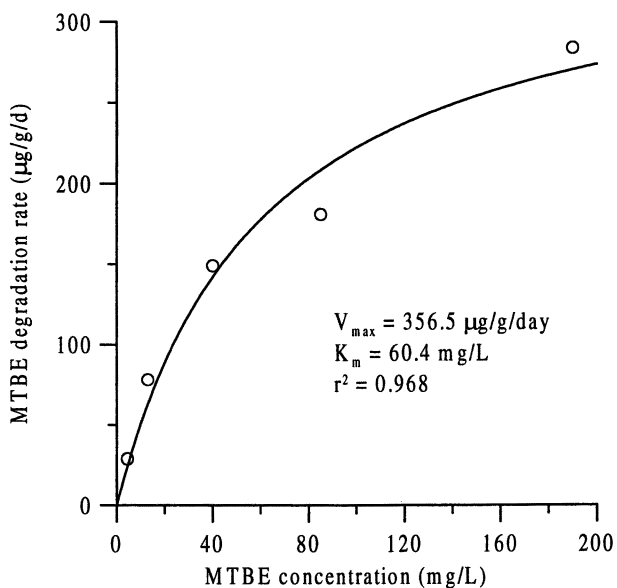
Figure 2: MTBE degradation kinetics exhibited by bed material taken from a fluidized bed bioreactor treating gasoline contaminated ground water
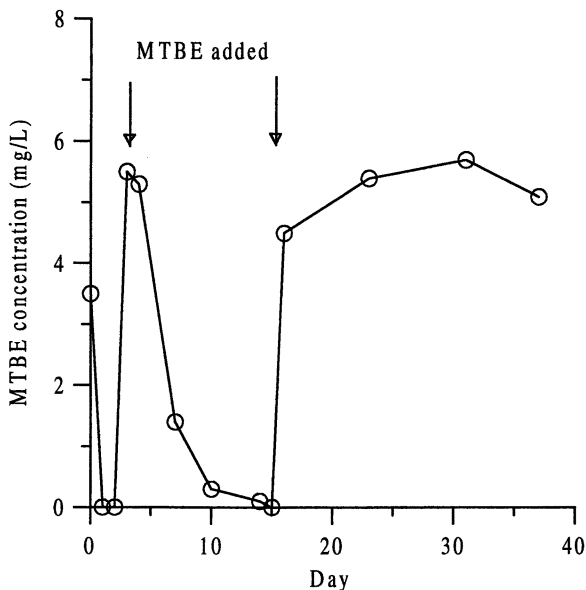
Figure 3: MTBE biodegradation activity declines over time when MTBE is supplied as a lone supplement

serving as an efficient energy source for this culture, as would be expected if MTBE degradation were a co-metabolic process. These results can be contrasted to those of Hanson *et al.* (*17*), where bacteria that grow on MTBE were able to maintain activity for an indefinite period.

It appeared from the evidence that co-metabolic biodegradation was the dominant mechanism for MTBE treatment in the field. With this realization, the focus of this research shifted to determining what supplemental carbon sources could serve as co-metabolites for MTBE degradation. Two approaches were taken. In one approach, bacteria were enriched from the field reactors on different carbon sources and then tested for their ability to degrade MTBE. In the second approach, bed material that had lost MTBE degradation activity was tested for MTBE degradation with and without an additional carbon source, to determine if the addition of the carbon source stimulated MTBE removal. A number of carbon substrates were tried as both supplements and as enrichment media, including toluene, p-xylene, methanol, *tert*-butyl alcohol, hexane, *iso*-pentane, lactate, acetate, glycerol, and glucose.

Enrichment cultures grown on *iso*-pentane consistently demonstrated MTBE degradation activity (Figure 4). MTBE degradation appears to be a constant characteristic of *iso*-pentane degraders. This result is consistent with the results of experiments conducted by others (*23, 25*).
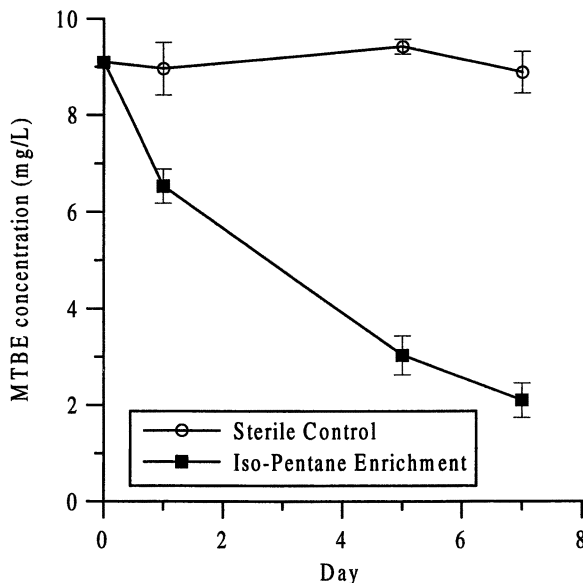
Figure 4: Degradation of MTBE by an iso-pentane enrichment. Mean plotted with error bars of one standard deviation

In the stimulation experiments, the fatty acids lactate and acetate were found to restore or enhance MTBE removal by bed material. The stimulation of MTBE removal by fatty acids was a surprising result, given that other general growth substrates, such as glycerol and glucose, did not stimulate MTBE degradation. Laboratory experiments were conducted with lactate under a variety of conditions. The use of lactate in combination with ferrous iron addition was particularly effective for stimulating MTBE removal. The combination of lactate and reduced iron is typically used for the cultivation of iron-bacteria, which are part of the microbial community in the fluidized bed bioreactors.

A field test was conducted in Nevada to determine if lactate could be used to stimulate MTBE treatment efficiency in a full-scale reactor. Lactate was added continuously at an average concentration of 20 mg/L to one reactor for a 21 day period. The MTBE treatment efficiency of the treated reactor was compared to the (control) reactor that did not receive lactate. The reactor that received lactate demonstrated a stimulation of MTBE removal efficiency in comparison to the reactor that did not receive lactate (Figure 5). However, the stimulation of MTBE removal by lactate addition was only transitory under these conditions. It is believed that lactate is not sufficiently selective for MTBE degraders and that, as lactate addition continues, MTBE degrading bacteria are over-grown by other microorganisms that can also use lactate, but do not

degrade MTBE. Further research on the use of lactate as a stimulant of MTBE degradation is focusing on the use of lactate in combination with *iso*-pentane and other alkanes.
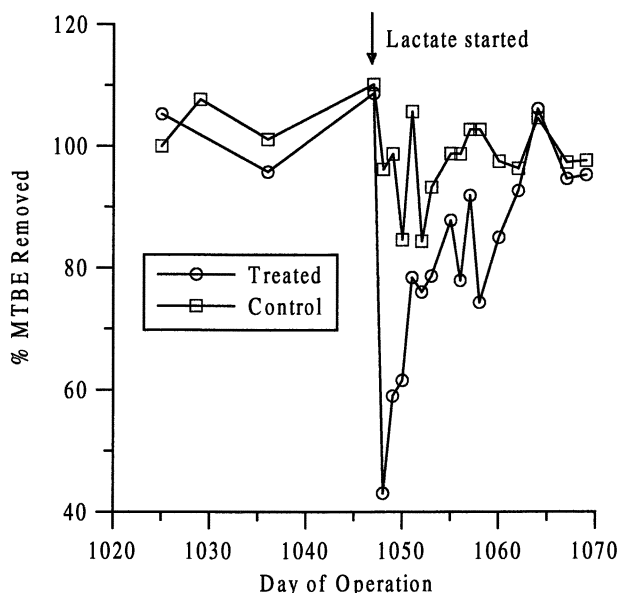
Figure 5. Lactate stimulation of MTBE removal efficiency in a full-scale reactor. Lactate addition caused a transitory improvement in MTBE treatment.

Experiments and field tests are being conducted to examine the use of *iso*-pentane as a co-substrate for MTBE degradation. Tests in laboratory reactors have shown that *iso*-pentane addition can stimulate MTBE removal (Figure 6). The impact of *iso*-pentane stimulation is greatest in poor performing reactors and is dose dependent (data not shown). Field tests of *iso*-pentane as a stimulant for MTBE biodegradation are being conducted.

Summary and Conclusions

Laboratory and field data support the argument that the primary mechanism for MTBE removal in fluidized-bed reactors treating contaminated groundwater containing gasoline hydrocarbons will be co-metabolic biodegradation. Gasoline range alkanes, particularly *iso*-pentane, can serve as reliable co-substrates for the stimulation of MTBE biodegradation. Other substrates, specifically lactate and acetate, can also stimulate MTBE degradation. However, application of lactate

as a co-substrate under field conditions is problematic, because lactate does not specifically enrich for MTBE degraders. Future research will focus on the use on *iso*-pentane as a co-substrate under field conditions and the use of lactate in combination with alkanes.
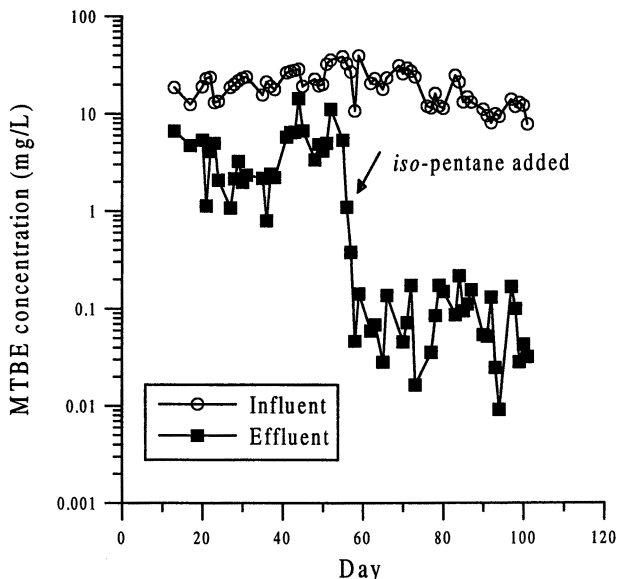
Figure 6: Iso-pentane stimulation test in laboratory reactor. Iso-pentane was added as a slug dose over two days.

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Appendix A

Physical Properties of Fuel Oxygenates and Additives

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The use of oxygenates in gasoline formulations and the subsequent release of these compounds to the environment has lead to interest in the physical properties of oxygenates and other gasoline constituents. Knowledge of a compound's physical properties and chemical structure enables one to predict its behavior in the environment and identify potential cleanup methods. Often environmental data from actual release sites is unavailable for compounds in production or being researched and developed for future use. In these instances the only data available to evaluate the behavior of a compound is published physical property data obtained by laboratory measurements or predictive calculations. This appendix compiles the available data for fuel oxygenates and additives. The appendix consists of four tables that list the physical properties of the common alkyl ethers (Table 1), alkyl ethers being developed for use in fuel formulations (Table 2), alkyl alcohols (Table 3), and aromatic compounds (Table 4). The one ester, tert-Butyl Formate appears in Table 2.

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TABLE 1. ALKYL ETHERS

Properties	Methyl tert-Butyl Ether MTBE	tert-Amyl Methyl Ether TAME	Ethyl tert-Butyl Ether ETBE	tert-Amyl Ethyl Ether TAEE	Diisopropyl Ether DIPE
Chemical Class	Ether	Ether	Ether	Ether	Ether
CAS No.	1634-04-4	994-05-08	637-92-3	919-94-8	108-20-3
CRC No. (81st Ed.)	10072	3396	10040	3375	10120
Merck No. (12th Ed.)	6111	654	3821	N/A	5231
Formula	$C_5H_{12}O$	$C_6H_{14}O$	$C_6H_{14}O$	$C_7H_{16}O$	$C_6H_{14}O$
Structural Formula	$CH_3OC(CH_3)_3$	$C_2H_5C(CH_3)_2OCH_3$	$(CH_3)_3COC_2H_5$	$C_2H_5C(CH_3)_2OC_2H_5$	$(CH_3)_2CHOCH(CH_3)_2$
Molecular Weight	88.15	102.18	102.18	116.2	102.18
Melting Point (°C)	-108.6 (16) -108.60 (10) -109 (4)	-----	-94 (16)	-----	-60 (24) -85.5 (19) -85.50 (10, 19) -86 (19, 27) -86.8 (16)
Boiling Point (°C)	53.6 - 55.2 (23, 30) 55 (12, 13, 14) 55 - 56 (1) 55.2 (4, 10, 12, 16, 26)	85 - 86 (1) 86 (13, 14, 30) 86.3 (4, 12, 16, 26) 86-87 (12)	67 (30) 69 - 71 (4) 72 (14) 72.2 (12, 26) 72.6 (16)	101 (12, 13, 14) 101 - 102 (12) 102 (16, 26)	68 (13, 19) 68 - 69 (1, 30) 68.2 (26) 68.30 (10) 68.34 (19)

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Continued on next page.

In Oxygenates in Gasoline; Diaz, A., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2001.

Table 1. *Continued*

Properties	MTBE	TAME	ETBE	TAEE	DIPE
Boiling Point (°C) ...continued	-----	-----	72.8 (4) 73 (12, 13) 73.1 (4)	-----	68.5 (16) 68.51 (19) 69 (19, 27) 91 (19, 30)
Liquid Density (g/cm³ @ 20°C)	0.74 (26) 0.7404 (4, 25) 0.7404 - 0.7578 (23) 0.7405 (11, 12, 16) 0.744 (23, 30) 0.735 @25°C (29) 0.7352 @25°C (12) 0.740 @25°C (1) 0.7460 @15.6°C (13)	0.764 (5) 0.77 (26, 30) 0.7656 @25°C (12) 0.770 @25°C (1) 0.7703 (4, 12, 16) 0.7758 @15.6°C (13)	0.73 (30) 0.74 (26) 0.7404 (4, 12) 0.7353 @25°C (12) 0.736 @25°C (16) 0.7452 @15.6°C (13)	0.75 (26) 0.7657 (12) 0.751 @18°C (16) 0.7609 @25°C (12) 0.7705 @15.6°C (13)	0.71854 (19) 0.7239 (19) 0.7241 (16) 0.73 (26) 0.7360 (19) 0.721 @25°C (29) 0.725 @25°C (1) 0.7289 @15.6°C (13) 0.73 @ 10°C (27) 0.736 - 0.7491 (30)
Water Solubility (mg/l)	42,000-54,300 (3) 43,000 (15) 43,000-54,300 (23, 30) 48,000 (4, 12, 13, 26) 50,000 (30) 51,260 (25) soluble (16)	11,500 (4, 12, 13) 12,000 (26) ~20,000 (30)	7,650 (30) 12,000 (4, 12, 13, 26) 26,000 (15) insoluble (16)	4,000 (12, 13)	2,000 (26) 2,039 (19, 30) 4,900 (19) 9,000 @ 20°C (19, 27, 30) 12,000 @20°C (19) slightly soluble (16)
Solubility in EtOH	very soluble (16)	very soluble (16)	very soluble (16)	very soluble (16)	miscible (16)

Properties	MTBE	TAME	ETBE	TAEE	DIPE
Vapor Pressure (mm Hg, 25°C)	240 (26) 245 (4, 12, 25) 245 - 251 (23) 245 - 256 (30) 250 (11) 251 (3)	68.3 (30) 75 (4, 12, 26)	130 (4, 12, 26) 152 (30)	50 (12)	149.11 (19) 150.71 (19) 159 (26) 130 @20°C (27) 149-151 @20°C (30)
Vapor Density (Air = 1)	3.1 (26) 3.80 (20)	3.6 (26)	3.6 (26)	4.0 (26)	3.52 (27) 3.6 (26)
Log Koc @25°C	0.55 - 0.91 (26) 1.01 (11) 1.035 (30) 1.04 (25) 1.049 (30) 1.05 (22, 23) 1.09 (25) 1.091 (17) 1.91 (30)	1.27 (30) 2.2 (30)	0.95 (30) 2.2 (30)	------	1.13 (26) 1.46 (30) 1.82 (30)
Log Kow @25°C	0.94 - 1.30 (23, 26) 0.94 (19, 29) 1.01 (19) 1.06 (19) 1.16 (19) 1.20 (23, 30) 1.23 (11)	1.55 (22)	1.74 (30)	------	1.52 (19, 26, 29, 30) 1.56 (19) 1.95 (19) 2.03 (19)

Continued on next page.

Table 1. *Continued*

Properties	MTBE	TAME	ETBE	TAEE	DIPE
Log Kow @25°C ...continued	1.24 (22, 25) 1.3 (19)	-----	-----	-----	-----
Henry's Law Constant (atm-m³/mol) @25°C	1.41E-04 (19) 5.28E-04 (23) 5.28E-4 – 3E-3 (26) 5.4106E-04 (29) 5.5E-04 (25) 5.87E-04 (19, 23, 30) 5.9E-04 (22) 5.92E-04 (19) 6.59E-04 (11) 1.1E-03 (30) 1.4E-03 (23, 30) 3.00E-03 (17) 3E-03 (23, 30) 3.01E-03 (19)	1.27E-03 (30) 1.3E-03 (22) 1.95E-03 (26)	2.64E-03 (26) 2.66E-03 (30) 2.7E-03 (22)	-----	1.7593E-03 (29) 4.77E-03 (19, 26, 30) 5.87E-03 (19, 30) 9.97E-03 (19, 30)
Dimensionless Henry's Law Constant @25°C	1.226E-01 (23, 30) 2.16E-02 (23) 2.2E-2 – 1.2E-1 (26) 2.399E-02 (23, 30) 2.6E-02 (17) 2.7E-02 (30) 4.496E-02 (30)	5.191E-02 (30) 8.1E-02 (26)	1.087E-01 (30) 1.1E-01 (26)	-----	1.95E-01 (30) 1.99E-01 (26) 2.399E-01 (30) 4.075E-01 (30)

Properties	MTBE	TAME	ETBE	TAEE	DIPE
Dimensionless Henry's Law Constant @25°C ...continued	5.772E-02 (23, 30) 1.8E-02 @20°C (23, 30)	-----	-----	-----	-----
Flash Point (°C)	-26 (13) -27.78 (10, 29) -28 (4) -30 (3) -32 (1)	-11 (1, 13)	-19 (13)	-----	-12 (1, 13) -27.78 (10, 29)
Amount in Gasoline (W%O$_2$/V%O$_2$)	2% / 11.0% (7, 20) 2.7% / 15.0% (7, 20, 28) 2.74% / 15% (6)	2% / 12.8% (7) 2.7% / 16.6% (6) 2.7% / 16.7% (28) 2.7% / 17.25% (7)	2.0% / 12.6% (20) 2.0% / 12.8% (7) 2.7% / 17.0% (20) 2.7% / 17.1% (6) 2.7% / 17.4% (28)	2.7% / 19.3% (28)	-----
Research Octane Number (RON)	117 (14) 118 (6, 22) 119 (7)	112 (6, 7, 14)	118 (6, 14, 22) 119 (6, 7)	105 (8, 14)	110 (22)
Motor Octane Number (MON)	101 (14) 103 (7)	98 (14) 99 (7)	101 (14) 103 (7)	95 (14) 112 (8)	-----
Blending Octane No. (R+M)/2	109 (4, 9) 110 (13) 111 (7) 118 (17)	105 (4, 9, 13) 105.5 (7)	110 (4, 9) 111 (7, 13)	100 (13) 109 (9)	107 (13)

Table 1. *Continued*

Properties	MTBE	TAME	ETBE	TAEE	DIPE
Neat RVP (psi) 100°F	7.8 (4, 14)	2.5 (4, 14)	4.0 (4, 14)	1.2 (14)	-----
Blending RVP (psi)	7.8 psi (14) 8 psi (4, 13) 8 psi / 55 kPa (13) 8-10 psi (9)	2 (13) 2 psi / 14 kPa (13) 2.5 psi (4, 14) 3-5 psi (9)	4 (4, 13) 4 psi / 28 kPa (13) 3-5 psi (9)	0 - 2 psi (9) 1.2 psi (14) 2 (13) 2 psi / 14 kPa (13)	0.7 (13) 0.7 psi / 5 kPa (13)
Oxygen (W%)	18.15 (6, 13) 18.2 (9)	15.66 (6, 13) 15.7 (9)	15.66 (6, 13) 15.7 (9)	13.77 (13) 13.8 (9)	15.66 (13)
Odor Threshold in Air (mg/m³)	0.32 - 0.47 (25) 5 - 53 ppb (3) 53 ppbv (11) 300 ppbv (11)	-----	-----	-----	0.10 (27)
Odor Threshold in Water (ug/L)	15 - 40 (2) 15 - 180 (21) 45 (11, 20) 95 (20)	194 (20)	49 (20)	-----	-----
Taste Threshold in Water (ug/L)	10 - 100 (3) 39 (11, 20) 40 - 140 (2) 134 (20) 24 – 135 ppb (21)	128 (20)	47 (20)	-----	-----
Odor Character	terpene like, ether, alcohol (11) sweet (27)	-----	-----	-----	sweet, pleasant (27)

Properties	MTBE	TAME	ETBE	TAEE	DIPE
USEPA Drinking Water Health Advisory or MCL	20-40ug/L	-----	-----	-----	-----
California DHS Primary MCL	13 ppb	-----	-----	-----	-----
Secondary MCL	5 ug/L	-----	-----	-----	-----
Action Level	13 ug/L	-----	-----	-----	-----
Uses	gasoline octane booster (4)	fuel additive for gasoline; gasoline octane booster (4)	gasoline additive (4)	-----	solvent for oils, waxes, and resins; paint and varnish removers (27)

TABLE 2: ALKYL ETHERS

Properties	tert-Hexyl Ethyl Ether THxEE	tert-Heptyl Ethyl Ether THpEE	tert-Hexyl Methyl Ether THxME	tert-Heptyl Methyl Ether THpME	Dimethyl Ether DME	Tert-Butyl Formate TBF
Chemical Class	Ether	Ether	Ether	Ether	Ether	Ester
CAS No.	5756-43-4	103-44-6	4747-07-3	629-32-3	115-10-6	762-75-4
CRC No. (81st Ed.)	-----	-----	-----	-----	7523	-----
Merck No. (12th Ed.)	-----	-----	-----	-----	6148	-----
Formula	$C_8H_{18}O$	$C_9H_{20}O$	$C_7H_{16}O$	$C_8H_{18}O$	C_2H_6O	$C_5H_{10}O_2$
Structural Formula	$C_3H_7C(CH_3)_2OC_2H_5$	$C_4H_9C(CH_3)_2OC_2H_5$	$C_3H_7C(CH_3)_2OCH_3$	$C_4H_9C(CH_3)_2OCH_3$	CH_3OCH_3	$(CH_3)_3COCHO$
Molecular Weight	130.23	144.26	116.20	130.23	46.07	102.13
Melting Point (°C)	-----	-68.3 (16)	-----	-----	-138.5 (5, 19) -141 (1) -141.49 (10, 19) -141.5 (5, 16) -141.50 (4)	-----
Boiling Point (°C)	143 (16)	166 (16)	~110 (13) 110 - 115 (14) 113 (12) 126.1 (16)	130 - 135 (14) 151 (16)	-22 (5) -23.60 (19) -24.00 (19) -24.8 (1, 5, 16, 26) -24.82 (4)	82 (30)

Properties	THxEE	THpEE	THxME	THpME	DME	TBF
Boiling Point (°C) ...continued	-----	-----	-----	-----	-24.84 (10, 19)	-----
Liquid Density (g/cm³ @ 20°C)	0.7722 (16)	0.790 (16)	0.7815 (12) 0.7860 @15.6°C (13)	0.7862 (16)	0.66 (26) 0.6612 (19) 0.6689 (19) 0.655 @25°C (29)	0.886 (30)
Water Solubility (mg/l)	-----	-----	-----	-----	35,300 (24) 47,000 - 353,000 (5, 26) 47,483 (19) 71,000 (19) 270,876 (19) 292,479 (19) 353,000 (19) soluble (16)	~40,000 (30)
Solubility in EtOH	very soluble (16)	-----	-----	very soluble (16)	soluble (16)	-----
Vapor Pressure (mm Hg, 25°C)	-----	-----	-----	-----	758-5,086 @25°C (26) 4,450 (5, 24)	81 @20°C (30)
Vapor Density (Air = 1)	-----	-----	-----	-----	1.6 (26) 1.62 (5)	-----
Log Koc @25°C	-----	-----	-----	-----	-0.29 (26) 0.1 (26) 1.15 (24)	1.11 (30)

Table 2. *Continued*

Properties	THxEE	THpEE	THxME	THpME	DME	TBF
Log Kow @25°C	-----	-----	-----	-----	-0.188 (19) -0.27 (19) 0.1 @18°C (29) 0.10 (19) 0.12 (19) 0.23 (19)	-----
Henry's Law Constant (atm-m3/mol) @25°C	-----	-----	-----	-----	4.89E-4 - 9.97E-4 (26) 4.89E-04 (19) 7.4E-04 (19) 9.97E-04 (19) 1.04E-03 (19) 7.63E-03 (5) 6.6435E-04 @18°C (29)	2.72E-04 (30)
Dimensionless Henry's Law Constant @25°C	-----	-----	-----	-----	2.03E-2 - 4.15E-2 (26)	1.111E-02 (30)
Flash Point (°C)	-----	-----	-----	-----	-41 (4,5) -41.11 (29)	-----
Research Octane Number (RON)	(THxEE1) 105.9 (8) (THxEE2) 104.9 (8) (THxEE3) 101.4 (8)	-----	-----	-----	-----	

Properties	THxEE	THpEE	THxME	THpME	DME	TBF
Motor Octane Number (MON)	(THxEE1) 93.1 (8) (THxEE2) 91.9 (8) (THxEE3) 91.5 (8)	-----	-----	-----	-----	-----
Blending Octane No. (R+M)/2	(THxEE1) 100 (9) (THxEE2) 99 (9) (THxEE3) 96 (9)	-----	95 (13)	-----	-----	-----
Neat RVP (psi) 100°F	-----	-----	1 (14)	0.9 (14)	-----	-----
Blending RVP (psi)	-----	-----	1 (6) 1 psi / 7 kPa (13)	0.9 psi (14)	-----	-----
Oxygen (W%)	(THxEE1) 12.3 (9) (THxEE2) 12.3 (9) (THxEE3) 12.3 (9)	-----	13.77 (13) 13.8 (14)	12.3 (14)	-----	-----
Odor Character	-----	-----	-----	-----	slight ethereal odor (4)	-----
Uses	-----	-----	-----	-----	alternative diesel fuel (4)	-----

TABLE 3: ALKYL ALCOHOLS

Properties	Ethanol	Methanol	tert-Butyl Alcohol	tert-Amyl Alcohol	Isopropanol	Isobutanol
	EtOH	MeOH	TBA	TAA	IPA	IBA
Chemical Class	Alcohol	Alcohol	Alcohol	Alcohol	Alcohol	Alcohol
CAS No.	64-17-5	67-56-1	75-65-0	75-85-4	67-63-0	78-83-1
Formula	C_2H_6O	CH_4O	$C_4H_{10}O$	$C_5H_{12}O$	C_3H_8O	$C_4H_{10}O$
CRC No. (81st Ed.)	5672	7581	10389	3628	10335	10388
Merck No. (12th Ed.)	3806	6024	1577	7282	5227	5146
Molecular Structure	CH_3CH_2OH	CH_3OH	$(CH_3)_3COH$	$CH_3CH_2C(CH_3)_2OH$	$(CH_3)_2CHOH$	$(CH_3)_2CHCH_2OH$
Molecular Weight	46.07	32.04	74.12	88.15	60.10	74.12
Melting Point (°C)	-114 (27) -114.1 (4, 16, 29) -114.10 (10) -117 (27)	-97.6 (16) -97.68 (10, 29) -97.8 (4) -98 (27)	25 (27) 25 - 26 (1) 25.4 (16) 25.6 (4) 25.66 (10) 25.7 (4) 25.82 (29)	-8.8 (16) -9 (4) -11.9 (27) -12 (1)	-86 (27) -87.87 (29) -88.5 (4, 10) -89 (27) -89.5 (1,16)	-108 (1, 4, 10, 16, 27, 29)
Boiling Point (°C)	78 (1, 13) 78 - 79 (30) 78.2 (16)	64.6 (16) 64.7 (4, 29, 30) 64.70 (10)	80 - 83 (13) 82.4 (16, 26) 82.41 (4)	101.8 (27) 102 (1, 22) 102.4 (16)	82 (13) 82.2 (22) 82.26 (10, 29)	107.03 (29) 107.66 (10) 107.8 (16)

Properties	EtOH	MeOH	TBA	TAA	IPA	IBA
Boiling Point (°C) ...continued	78.29 (10, 29) 78.3 (22) 78.4 (27) 78.5 (4, 26)	65 (13, 27)	82.42 (10, 29) 82.9 (30) 83 (1, 27)	102.5 (4)	82.3 (16) 82.4 (1, 27) 82.5 (4)	107.9 (22, 27) 108 (1, 4)
Liquid Density (g/cm^3 @ 20°C)	0.789 (4) 0.7893 (16) 0.79 (26, 27) 0.794 (30) 0.787 @25°C (29) 0.790 @25°C (1) 0.7939 @15.6°C (13)	0.7914 (16) 0.7915 (4) 0.796 (30) 0.787 @25°C(29) 0.7963 @15.6°C (13) 0.8 @15°C (27)	0.78 (27) 0.78581 (4) 0.7887 (16) 0.79 (26) 0.791 (30) 0.775 @25°C (1) 0.7899 @15.6°C (13)	0.805 (22) 0.8084 (4) 0.809 (27) 0.8096 (16) 0.805 @25°C (1)	0.78 (27) 0.78505 (4) 0.789 (22) 0.7809 @25°C (16) 0.7810 @15.6°C (13) 0.783 @25°C(29) 0.785 @25°C (1)	0.80 (27) 0.8018 (16) 0.802 (22) 0.797 @25°C (29) 0.803 @25°C (1) 0.806 @15°C (4)
Water Solubility (mg/l)	miscible (16)	miscible (16)	miscible (16)	140,000 @30°C (27) soluble (16)	miscible (16)	68,200 (22) 95,000 @18°C (27) slightly soluble (16)
Solubility in EtOH	miscible (16)	miscible (16)	miscible (16)	------	miscible (16)	soluble (16)
Vapor Pressure (mm Hg, 25°C)	44 (26) 49 - 56.5 (30) 50 (27) 43.9 @20°C (27)	121.58 (30) 126 (18) 92 @20°C (27)	40 - 42 (30) 41 (26) 42 (27)		32 @20°C (27) 57 @30°C (27)	10 (27)

Table 3. *Continued*

Properties	EtOH	MeOH	TBA	TAA	IPA	IBA
Vapor Density (Air = 1)	1.6 (26, 27)	1.1 (27) 1.11 (4)	2.55 (27) 2.6 (26)	------	2.07 (27) 2.1 (5)	2.55 (27)
Log Koc @25°C	-0.14 (26) 0.2 (30) 1.21 (30) 1.77 (22)	0.44 (30) 0.921 (30) 0.95 (22)	0.37 (27) 1.57 (26, 30)	------	1.4 (22)	0.95 (22)
Log Kow @25°C	-0.16 (30) -0.31 (29, 30) -0.32 (26, 27)	-0.66 (27) -0.75 (30) -0.77 (22, 29) -0.82 (27)	0.35 (26, 29, 30)	0.89 (22, 27)	0.05 (22, 29)	0.65 (27) 0.76 (22, 29) 0.83 (27)
Henry's Law Constant (atm-m³/mol, 25°C)	5.13E-06 (30) 5.2E-06 (22) 6.17E-06 (30) 6.29E-06 (30) 8.1083E-06 (29)	4.42E-06 (30) 4.55E-06 (18) 4.6E-06 (22) 5.1932E-06 (29)	1.04E-05 (30) 1.175E-05 (30) 1.19E-05 (30) 1.21E-05 (26) 1.4E-05 (22) 1.47E-05 (30) 1.7279E-05 (29)	------	7.90E-06 (22) 1.2408E-05 (29)	1.1796E-05 (29) 1.2E-05 (22)
Dimensionless Henry's Law Constant	2.097E-04 (30) 2.1E-04 (17) 2.52E-04 (17) 2.522E-04 (30) 2.57E-04 (27) 2.571E-04 (30)	1.087E-04 (30) 1.91E-04 (27)	4.251E-04 (30) 4.80E-04 (30) 4.803E-04 (30) 4.864E-04 (30) 4.90E-04 (27) 5.03E-04 (26) 5.927E-04 (30)	5.62E-04 (27)	3.47E-04 (27)	------

Properties	EtOH	MeOH	TBA	TAA	IPA	IBA
Flash Point (°C)	12.78 (10, 29) 13 (4, 13) 16 (1)	11 (13) 11.11 (10, 29) 12 (4)	11 (1, 13) 11.1 (4) 11.11 (10, 29)	19 (4) 21 (1)	11 (1) 11.67 (10, 29) 11.7 (4) 12 (13)	27 (1) 27.78 (10, 29) 28 (4)
Amount in Gasoline (W%O$_2$/V%O$_2$)	2.0% / 5.7% (7,20) 2.7% / 7.5% (28) 2.7% / 7.7% (7,20) 3.5%/10.0%(7, 20) 3.7% / 10% (6)	variable (28)	2.7% / 11.8% (28)	-----	2.7% / 9.6% (20)	-----
Research Octane Number (RON)	111 (17) 129 (6,7) 130 (22)	133 (22)	109 (22)	-----	121 (22)	106 (22)
Motor Octane Number (MON)	96 (7) 102	105	100	-----	98	-----
Blending Octane No. (R+M)/2	112.5 (7) 113 (4, 9) 115 (13) 129 (17)	116 (9) 119 (13)	97 (13) 101 (4, 9)	-----	106 (13)	-----
Neat RVP (psi) 100°F	2.3 (4)	-----	1.7 (4)	-----	-----	-----
Blending RVP (psi)	14 psi (17) 18 (4, 13) 18 psi/124kPa(13) 17 - 22 psi (9)	40 (13) 40 psi / 276 kPa (13) 31 - 60 psi (9)	9 (4, 13) 9 psi / 62 kPa (13) 10 - 15 (9)	-----	14 (13) 14 psi / 97 kPa (13)	-----

Table 3. *Continued*

Properties	EtOH	MeOH	TBA	TAA	IPA	IBA
Oxygen (W%)	34.7 (9) 34.73 (13)	49.33 (13) 49.9 (9)	21.3 (13) 21.6 (9)	-----	26.62 (13)	-----
Odor Character					sharp, musty (27)	sweet, musty (27)
Odor Threshold in Air (mg/m³)	-----	-----	-----	8.42 (27) 30.03 (27)	1,750 (27)	-----
Taste Threshold in Water (ug/L)	.-----	10 – 20,000 (18)	-----	-----	-----	-----
Odor Character	-----	-----	camphor-like odor (4)	EtOH	MeOH	TBA
California DHS Action Level	-----	-----	12 ppb	-----	-----	-----
Uses	gasoline octane booster (4)	EtOH denaturant (27) gasoline octane booster; ingredient of gasoline and diesel oil fuels; EtOH denaturant (4)	EtOH denaturant, gasoline octane booster (4) as blending agent up to 7% to increase octane rating of unleaded gasoline (27) anti-icing additive (27)	-----	de-icing agent for liquid fuels (27) EtOH denaturant (4)	-----

TABLE 4: AROMATIC COMPOUNDS

Properties	Benzene	Toluene	Ethyl Benzene	m-Xylene	o-Xylene	p-Xylene
Chemical Class	Aromatic	Aromatic	Aromatic	Aromatic	Aromatic	Aromatic
CAS No.	71-43-2	108-88-3	100-41-4	108-38-3	95-47-6	106-42-3
Formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}	C_8H_{10}
CRC No. (81st Ed.)	867	1947	1668	1453	1452	1454
Merck No. (12th Ed.)	1094	9667	3812	10214	10214	10214
Molecular Weight	78.11	92.14	106.17	106.17	106.17	106.17
Melting Point (°C)	5.5 (1, 4, 16) 5.53 (10, 29)	-93 (1) -94.9 (16) -94.97 (10, 29) -95 (4)	-94.9 (16) -94.95 (10, 29) -95 (1) -95.01 (4)	-47.4 (4) -47.8 (16) -47.85 (10, 29)	-25 (4) -25.17 (10, 29) -25.2 (16) -25 to -23 (1)	12 - 13 (1) 13 - 14 (4) 13.2 (16) 13.25 (10) 13.26 (29)
Boiling Point (°C)	80 (1) 80.0 (16) 80.09 (10, 29) 80.1 (4, 23, 30)	110.6 (1, 4, 16, 30, 23) 110.63 (10, 29)	136 (1) 136.1 (16) 136.20 (10, 29) 136.25 (4, 23, 30)	138 - 139 (1) 139.1 (16) 139.12 (10, 29) 139.3 (4, 23, 30)	143 - 145 (1) 144 (4) 144.4 (23, 30) 144.43 (10, 29) 144.5 (16)	137-138 (4, 23,30) 138 (1) 138.3 (16) 138.36 (10, 29)
Liquid Density (g/cm³ @ 20°C)	0.8786 (30) 0.88 (23, 30) 0.873 @25°C(29)	0.866 (4) 0.865 @25°C (1, 29)	0.867 (23, 30) 0.8670 (16) 0.865 @25°C(29)	0.8642 (16) 0.8842 (23, 30) 0.861 @25°C(29)	0.8801 (4) 0.8802 (23, 30) 0.870 @25°C (1)	0.86104 (4) 0.858 @25°C(29) 0.8611 (16, 23, 30)

Table 4. *Continued.*

Properties	Benzene	Toluene	Ethyl Benzene	m-Xylene	o-Xylene	p-Xylene
Liquid Density (g/cm^3 @ 20°C) ...continued	0.874 @25°C (1) 0.8765 (16, 23) 0.8787 @15°C(4)	0.8669 (16, 23, 30)	0.867 @25°C (1)	0.868 @25°C (1) 0.8684 @15°C(4)	0.876 @25°C(29) 0.8802 @10°C (16)	0.866 @25°C (1)
Water Solubility (mg/l)	1,780 (23,30) 1,791 (23) slightly soluble (16)	534.8 (23, 30) insoluble (16)	161 (23,30) insoluble (16)	146 (23,30) insoluble (16)	175 (23,30) insoluble (16)	156 (23, 30) insoluble (16)
Solubility in EtOH	miscible (16)	miscible (16)	miscible (16)	miscible (16)	miscible (16)	miscible (16)
Vapor Pressure (mm Hg, 25°C)	76 (30) 95.19 (23,30)	28.4 (23, 30)	9.53 (23, 30)	8.3 (23, 30)	6.6 (23, 30)	8.7 (23, 30)
Vapor Density (Air = 1)	3.36 (20)	3.97 (20)	4.57 (20)	------	4.57 (20)	------
Log Koc @25°C	1.1 - 2.5 (23) 1.50 - 2.16 (30) 1.8 - 1.99 (30) 1.92 @20°C (29)	1.56 - 2.25(23,30) 2.48 @20°C (29)	1.98 - 3.04(23,30) 2.94 (30) 2.72 @20°C (29)	2.04 - 3.15(23,30) 2.20 (30) 2.72 @20°C (29)	1.68 - 1.83(23, 30) 2.72 @20°C (29)	2.05 - 3.08(23,30) 2.31 (30) 2.72 @20°C (29)
Log Kow @25°C	1.56 - 2.15(23,30) 2.13 (23, 29, 30)	2.11 - 2.80(23,30) 2.73 (23, 29, 30)	2.68 – 3.26 (23) 3.15 (23, 29, 30)	3.09 – 3.37 (23) 3.2 (29) 3.20 (23,30)	2.77 - 3.12 (23,30) 3.12 (23, 29, 30)	3.08 - 3.29(23, 30) 3.15 (23, 29, 30)
Henry's Law Constant (atm-m^3/mol, 25°C)	5.43E-03 (23, 30)	5.94E-03 (23, 30) 6.3522E-03 (29)	8.1413E-03 (29) 8.44E-03 (23, 30) 6.60E-03 – 8.75E-03 (23)	6.7775E-03 (29) 7.68E-03 (23, 30)	4.1895E-03 (29) 5.1E-03 (23, 30)	6.1547E-03 (29) 7.68E-03 (23, 30)

Properties	Benzene	Toluene	Ethyl Benzene	m-Xylene	o-Xylene	p-Xylene
Dimensionless Henry's Law Constant	2.219E-01 (23,30) 0.22 (30)	2.428E-01 (23,30)	3.45E-01 (23, 30) 2.89E-01 – 3.83E-01 (23)	3.139E-01 (23,30)	2.084E-01 (23,30)	3.139E-01 (23,30)
Flash Point (°C)	-11 (1, 4) -11.11 (10, 29)	4 (1) 4.4 (4, 29) 4.44 (10)	15 (10, 29) 18 (4) 22 (1)	25 (1, 4, 10, 29)	17 (4) 17.22 (10, 29) 32 (1)	25 (1, 4, 10, 29)
Amount in Gasoline	up to 3% (2)	-----	-----	-----	-----	-----
Research Octane Number (RON)	123 (6)	-----	-----	-----	-----	-----
Blending RVP (psi)	3 psi (11)	1 psi (11)	-----	3 psi (11)	3 psi (11)	3 psi (11)
Oxygen (W%)	0	0	0	0	0	0
Taste Threshold in Water (ug/L)	~500 (2)	-----	-----	-----	-----	-----
USEPA Drinking Water MCL	5 ug/L	1,000 ug/L	700 ug/L	10,000 ug/L	10,000 ug/L	10,000 ug/L
California DHS Primary MCL	1ug/L	150 ug/L	700 ug/L	1750 ug/L	1750 ug/L	1750 ug/L
Uses	gasoline additive (4)	gasoline additive (4)	-----	-----	-----	-----

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Appendix B

Polar Fuel Constituents: Compound Identification and Partitioning between Nonaqueous-Phase Liquids and Water

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Spills and leakages of fuels to the ground often lead to Non-Aqueous Phase Liquids (NAPLs) on top of the ground water table. As a first step to assess the impact of fuel related contaminants on groundwater quality due to point source releases, it is essential to *identify* fuel constituents that partition readily into water and to *quantify* their partitioning from NAPL into groundwater. Such data are available for major fuel constituents, including BTEX (*1, 2, 3, 4*), methyl tert-butyl ether (MTBE) (*1*) and PAH (*5, 6*).

In contrast, the identity and partitioning of other, polar compounds present in fuels have been neglected in spill scenarios so far. Since such substances are expected to be mobile in the subsurface they may reach groundwater wells before classical fuel related contaminants (e.g. BTEX) are detected. A list of polar fuel constituents is given in Table 1. Apart from the fuel oxygenates (ethers and alcohols) typical European and American gasolines contain a variety of other polar compounds, including anilines, phenols and pyridines, which are present in gasoline at concentrations ranging from 1 to 100 mg/L.

Table 1 also contains partitioning data of the solutes between various organic phases (gasoline, isooctane, 1-octanol) and water. The fuel-water partitioning coefficient is defined as

$$K_{fw} = \frac{c_f}{c_w} \qquad [-]$$

c_f and c_w are the equilibrium concentrations of a solute in fuel and water phase, respectively. K_{iw} and K_{ow} are defined accordingly. Thus, a high K value reflects a compound's low tendency to partition from the respective organic phase into water and vice versa.

Table 1: Polar fuel constituents and their partitioning constants between non-aqueous phases and water[a]

Substance class	Substance	Reference	K_{fw} (Gasoline)[b]	K_{iw} (Isooctane)	K_{ow} (Octanol) [7, 8, 9]
Ether	Methyl tert-butyl ether (MTBE)	c	16 [g]	15 [i]	8.7
	Ethyl tert-butylether (ETBE)	c			
	Tert-amyl methyl ether (TAME)	c			
	Di-n-propylether	10			
Alcohols	Methanol	c	0.0051 [g]	0.0034 [g]	0.17
	Ethanol	c			
	2-Propanol	10			
	2-Butanol	10			
	Tert-butanol (TBA)	c			
	2-Ethoxyethanol	11			
	4-Hydroxy-2-methyl-2-pentanol	11			
	2-Butoxyethanol	11			
	1-(2-butoxyethoxy)ethanol	11			
Ketones	Acetone	10			
	2-Butanone	10			
	2-Pentanone	10			
Phenols	Phenol	10, 11, 12, 13	3.2	0.12	29
	2-Methylphenol	10, 11, 12	14	0.69	89
	3-Methylphenol	10, 11, 12, 13			
	4-Methylphenol	10, 11, 12	9.3	0.36	87

Phenols

2-Ethylphenol	*11, 12, 13*			
3-Ethylphenol	*11, 12*			
4-Ethylphenol	*10*			
2,3-Dimethylphenol	*10, 13*			
2,4-Dimethylphenol	*10*			
2,5-Dimethylphenol	*11, 12*	44	7.4	230
2,6-Dimethylphenol	*13*	22	0.98	170
3,4-Dimethylphenol	*10, 11, 12, 13*			
3,5-Dimethylphenol	*11, 12*			
2-Ethyl-5-methylphenol	*11, 12*			
3-Ethyl-5-methylphenol	*12*			
2,3,6-Trimethylphenol	*12*			
2,4,6-Trimethylphenol	*10, 12*	120	26	540
3,4,5-Trimethylphenol	*10, 12*	53	2.5	777 [m]
2-(1,1-dimethylethyl)-6-methylphenol	*11*			
4-(1,1-dimethylethyl)-2-methylphenol	*11*			
3,5-Bis(1-methylethyl)phenol	*11*			
C3-alkylphenol, not specified	*12*			
C8-alkylphenol, not specified	*13*			

Continued on next page.

Table 1 continued

Substance class	Substance	Reference	K_{fw} (Gasoline)[b]	K_{iw} (Isooctane)	K_{ow} (Octanol) (7, 8, 9)
Anilines	Aniline	10, 11, 12, 13	3.1	0.66	7.9
	2-Methylaniline	10, 11, 13	12	3.3 [k]	21
	3-Methylaniline	10, 12, 13			
	4-Methylaniline	10, 11, 12	12	2.0	25
	N-Methylaniline	11			
	2,4-Dimethylaniline	10			
	2,6-Dimethylaniline	10	39	16 [k]	160
	3,4-Dimethylaniline	10	29	5.6	110
	3,5-Dimethylaniline	10, 12			
Pyridines	2-Methylpyridine	11			
	2,3,5-Trimethylpyridine	11			
	3-Ethyl-5-methylpyridine	11			
	5-Ethyl-2-methylpyridine	11			
	3-Ethyl-2,6-dimethylpyridine	11			
Triazoles	Benzotriazole	d	0.2	0.15	27.5
	1-Methylbenzotriazole	d	2.7	0.42	13.5
Thiophenes	Thiophene	e	110	50	65
	Benzothiophene	e	1700	263 [l]	1300
	Benzene	f	350 [g]	115 [l]	130
	Toluene	f	1250 [g]	562 [l]	537

(a): K_{iw} and K_{ow} data only given if K_{fw} available

(b): premium gasoline (ROZ 98) containing 9 % MTBE, 43 % aromatics, K_{fw} data for *neutral* compounds

(c): common fuel oxygenates

(d): common fuel additives (corrosion inhibitors)

(e): residual sulfur compounds

(f): most water-soluble hydrocarbons in fuels

(g): from (*1*)

(i): calculated from (*14*)

(k): alkane-water partition constant from (*15*)

(l): hexane-water partition constant from (*16*)

(m): estimated with fragment method (*9*)

To date, only few K_{fw} values are available. Besides, K_{fw} values may vary significantly depending on the composition of the fuel (e.g., MTBE content). For *unpolar* solutes (only van-der-Waals interactions) this dependence is quite small and Kfw values can be estimated from K_{iw} or K_{ow} data (e.g., for BTEX). For *polar* solutes, including anilines and phenols, the effect is much more pronounced. In general, K_{fw} values of anilines and phenols decrease with decreasing MTBE content of fuels. For such compounds, K_{fw} values cannot be predicted accurately from K_{iw} or K_{ow}. Additional data and an in-depth discussion of the factors that govern the distribution of polar solutes between fuel and aqueous phase is given elsewhere (*10*).

All investigated anilines, phenols and benzotriazoles partition better from gasoline into water than benzene, the most water soluble hydrocarbon in gasoline. The K_{fw} for MTBE is comparable to methyl anilines and methyl phenols. As an example, a typical concentration of aniline in the investigated gasolines is 10 mg/L. The K_{fw} for aniline is 3.1, with a water/gasoline volume ratio of 1 this yields a concentration of aniline in the adjacent water phase of $c_w = 2.5$ mg/L.

The data presented here suggest that polar fuel components behave distinctly differently from known fuel constituents such as BTEX in a point source release scenario. As shown for aniline, the low K_{fw} for polar fuel constituents values imply that fuels in contact with groundwater will be efficiently extracted. This leads to a rapid depletion of such compounds in a NAPL, causing a transient composition of the contaminant plume with elevated aqueous concentrations of polar compounds at the leading edge of the plume.

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