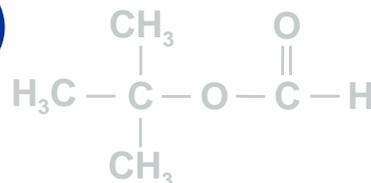| REPORT DOCUMENTATION PAGE		*Form Approved* *OMB No. 0704-0188*

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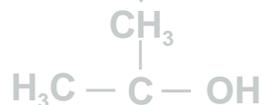
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14. ABSTRACT
This report summarizes the approach to be followed when evaluating the natural attenuation of MTBE and other fuel oxygenate and considers the consequences of the unique physical and chemical characteristics and their resultant behavior in the environment.

15. SUBJECT TERMS
MTBE, natural attenuation, fuel hydrocarbons, oxygenates, biodegradation, groundwater remediation, geochemistry, contaminant destruction rates

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FINAL

Methyl *tert* - Butyl Ether (MTBE)

MTBE

$$CH_3$$
$$CH_3$$
$$CH_3$$

$$H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - OH$$

t- Butyl Alcohol
(TBA)

$$CH_3 \qquad\qquad O$$
$$H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - O - \overset{\overset{\displaystyle O}{\|}}{C} - H$$

t- Butyl Formate
(TBF)

Its Movement and Fate in the Environment and Potential for Natural Attenuation

$$H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$$

Acetone

$$H_3C - \overset{\overset{\displaystyle}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH_3$$

2- Propanol

$$H_3C - \overset{\overset{\displaystyle O}{\|}}{C} - O - CH_3$$

Methyl Acetate
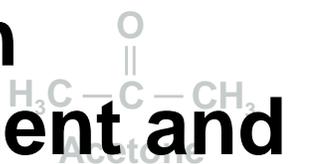
October 1999

**Air Force Center for
Environmental Excellence**

FINAL

Methyl *tert*-Butyl Ether (MTBE) –
Its Movement and Fate in the Environment
and
Potential for Natural Attenuation

Technical Summary Report
October 1999

Prepared For

Air Force Center for Environmental Excellence
Technology Transfer Division
Brooks Air Force Base
San Antonio, Texas

Prepared By

Parsons Engineering Science, Inc.
1700 Broadway, Suite 900
Denver, Colorado 80290

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ACRONYMS AND ABBREVIATIONS

μg/L	micrograms per liter
AFCEE/ERT	Air Force Center for Environmental Excellence, Technology Transfer Division
AMC	Air Mobility Command
API	American Petroleum Institute
atm-m^3/mol	atmospheric-cubic meters per mole
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
°C	degrees centigrade
CFB	Canadian Forces Base
cm/sec	centimeters per second
cm/yr	centimeters per year
DAI GC/MS	direct aqueous injection-gas chromatograph/mass spectrometer analytical method
DIPE	di-isopropyl ether
ETBE	ethyl *tert*-butyl ether
°F	degrees Fahrenheit
ft/day	feet per day
ft/yr	feet per year
ΔG°	Gibbs free energy of the reaction
GC	gas chromatograph
LTM	long-term monitoring
LUFT	leaking underground fuel tank
m/d	meters per day
MCLs	maximum contaminant levels
mg/L	milligrams per liter
MNA	Monitored Natural Attenuation
MTBE	methyl *tert*-butyl ether
mV	millivolts
NAPLs	nonaqueous-phase liquids
NDWCO	National Drinking Water Contaminant Occurrence Database
NWQA	National Water Quality Assessment
ORD	Offices of Research and Development
ORP	oxidation reduction potential
OSWER	Office of Solid Waste and Emergency Response
PAHs	polycyclic aromatic hydrocarbon compounds
ppb-v	parts per billion by volume
redox	reduction/oxidation
RFG	Reformulated Gasoline Program
SO$_4^2$	sulfate
TAME	*tert*-amyl methyl ether

TBA	*tert*-butyl alcohol
TBF	*tert*-butyl formate
TFH	total fuel hydrocarbons
TPH	total petroleum hydrocarbons
US	United States
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOCs	volatile organic compounds

SECTION 1

INTRODUCTION

This document was prepared by Parsons Engineering Science, Inc. under contract to the Air Force Center For Environmental Excellence, Technology Transfer Division (AFCEE/ERT) through the Air Mobility Command (AMC). The AFCEE document entitled *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (AFCEE Technical Protocol, 1995) presents a detailed approach for evaluating the natural attenuation of fuel hydrocarbons.

The approach to be followed when evaluating the natural attenuation of methyl *tert*-butyl ether (MTBE) and other fuel oxygenates should mirror that of the AFCEE Technical Protocol for fuel hydrocarbons (1995) with a few notable additions, which are a consequence of the unique physical and chemical characteristics of oxygenates and their resultant behavior in the environment. For example, MTBE is significantly more soluble, sorbs less, and is less likely to volatilize out of groundwater than the aromatic fuel constituents benzene, toluene, ethylbenzene, and xylene isomers (BTEX compounds). In addition, the mechanisms of biodegradation of the BTEX compounds and the evaluation of this biodegradation are fairly straightforward; this is not the case for MTBE.

Although it has been shown that MTBE can be biologically degraded under aerobic, denitrifying, Fe(III)-reducing, sulfate-reducing, or methanogenic conditions, in many cases MTBE remains biologically recalcitrant. Because biodegradation of BTEX and MTBE may occur via the same terminal electron-accepting processes, and because BTEX and MTBE are typically found in association, it is difficult to distinguish MTBE

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biodegradation from the biodegradation of other fuel hydrocarbon compounds using the relative depletion of electron acceptors, or the appearance of metabolic byproducts, as specified in the AFCEE Technical Protocol (1995).

The objectives of this document are to present an overview of the physical and chemical characteristics of the fuel oxygenate MTBE that influence its movement and fate in the environment, to summarize the literature regarding the results of field-scale and laboratory evaluation of the naturally-occurring breakdown ("degradation") of MTBE, and to provide recommendations for data collection and analysis in support of natural attenuation supplemented with long-term monitoring (LTM) for restoration of groundwater contaminated with MTBE. Specifically, this document is intended to evaluate the biodegradation potential of MTBE, and to describe those conditions under which natural attenuation of MTBE (not necessarily resulting from destructive attenuation processes, including biodegradation) may be a viable remedial option.

The US Environmental Protection Agency (USEPA) Offices of Research and Development (ORD) and Solid Waste and Emergency Response (OSWER) define monitored natural attenuation (MNA) as (USEPA, 1999):

> *the reliance on natural attenuation processes (within the context of a carefully controlled and monitored clean-up approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other, more active methods. The "natural attenuation processes" that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants."*

As suggested by this definition, the tendency for contaminants in groundwater to attenuate naturally is determined by a combination of the geological and hydrogeological site conditions, the physical and chemical properties of the particular contaminants of concern, and the continuing contribution of contaminants to the groundwater from contaminant sources.

Natural attenuation of contaminants results from the simultaneous action of several mechanisms that are classified as either destructive or nondestructive. Destructive processes include biodegradation, abiotic oxidation, and hydrolysis. The occurrence of destructive processes, including biodegradation, may be demonstrated by historical trends in site-related contaminant concentrations, areal distributions of geochemical indicators, and the presence of microbial populations capable of utilizing site-related contaminants as a substrate. Nondestructive attenuation mechanisms include sorption, dispersion, dilution from recharge, and volatilization.

Remediation by natural attenuation mechanisms is achieved when natural attenuation mechanisms bring about a reduction in the total mass of a contaminant dissolved in groundwater, or its concentration or mobility in the environment. In most cases, natural attenuation will reduce dissolved BTEX concentrations below regulatory standards such as maximum contaminant levels (MCLs) before the hydrocarbon plume reaches potential receptors. However, because of significant differences in the chemical properties of BTEX compounds and MTBE, this is not necessarily the case with dissolved MTBE plumes.

The AFCEE *Remediation Matrix - Hierarchy of Preferred Alternatives* (1994) has identified natural attenuation as the first option to be evaluated for remediation of contaminated groundwater at Air Force sites. This matrix implies only that natural attenuation should be evaluated prior to proceeding (if necessary) to more costly solutions (e.g., pump and treat), not that natural attenuation be selected "presumptively" in every case. To date, USEPA has not identified natural attenuation as a presumptive remedy.

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Advantages of MNA over conventionally-engineered remediation technologies include: 1) during natural attenuation, contaminants are ultimately transformed to innocuous byproducts (e.g., carbon dioxide and water), rather than being transferred to another phase or location within the environment; 2) natural attenuation is non-intrusive and allows continued use of infrastructure during remediation; 3) engineered remedial technologies can pose greater risk to potential receptors than natural attenuation because contaminants may be transferred to other receptor exposure points during remediation activities; 4) MNA is less costly than currently available remedial technologies such as pump-and-treat; 5) MNA is not subject to limitations imposed by the use of mechanized remediation equipment (e.g., no equipment down time); and 6) those fuel compounds that are the most mobile and toxic are generally the most susceptible to biodegradation.

Limitations of MNA include: 1) natural attenuation is subject to natural and institutionally-induced changes in local hydrogeologic or chemical conditions, including changes in groundwater gradients/velocity, pH, and electron acceptor concentrations, or potential future releases; 2) aquifer heterogeneity may complicate site characterization, as with any remedial technology; 3) certain compounds may be recalcitrant (resistant to naturally-occurring degradation processes); and 4) time frames for achieving remediation objectives may be relatively long.

This document evaluates the potential for natural attenuation of fuel hydrocarbon spills containing MTBE, and describes those processes that bring about natural attenuation. The document also provides recommendations for adapting typical site characterization activities, natural attenuation evaluations, and LTM protocols to deal with particular characteristics of MTBE. The objective of the work described herein is to support implementation of MNA at sites where naturally occurring subsurface attenuation processes are reducing dissolved fuel hydrocarbon and oxygenate concentrations to acceptable levels. A recent comment made by a member of the regulatory community sums up what is required to successfully implement MNA (National Research Council, 1993):

A regulator looks for the data necessary to determine that a proposed treatment technology, if properly installed and operated, will reduce the contaminant concentrations in the soil and water to legally mandated limits. In this sense the use of biological treatment systems calls for the same level of investigation, demonstration of effectiveness, and monitoring as any conventional [remediation] system.

To support implementation of MNA, the proponent must scientifically demonstrate that degradation of site contaminants is occurring at rates sufficient to be protective of human health and the environment. Three basic lines of evidence can be used to support natural attenuation including:

1. Documented loss of contaminants or decreases in concentrations at the field scale,

2. The use of contaminant and geochemical analytical data, and

3. Direct microbiological evidence.

The first line of evidence involves demonstrating that a reduction in the total mass of contaminants, or long-term decreases in contaminant concentrations, are occurring at the site. The second line of evidence involves the use of geochemical analytical data to demonstrate that a decrease in contaminant and electron acceptor concentrations can be related to increases in metabolic byproduct concentrations. The third line of evidence, direct microbiological evidence, can be used to show that indigenous biota are capable of degrading site contaminants.

At a minimum, the first two lines of evidence listed above should be used in the natural attenuation demonstration. To further document natural attenuation, direct microbiological evidence can be used. Microbiological evidence may be particularly appropriate in the case of MTBE, because biodegradation of MTBE can be difficult to

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document at the field scale. Such a "weight-of-evidence" approach will greatly increase the likelihood of successfully implementing MNA at sites where natural processes are restoring the environmental quality of groundwater contaminated with fuel hydrocarbons and oxygenates.

This document contains five sections, including this introduction, and six appendices. The history of development and use of MTBE are described in Section 2, together with a discussion of the physical and chemical properties of MTBE that influence its movement and fate in the environment, and a summary of the literature related to MTBE biodegradation. Section 3 presents considerations specific to MTBE that must be addressed in obtaining scientific data to support the natural attenuation option. Conclusions and recommendations are summarized in Section 4, and Section 5 presents the references used in preparing this document.

Appendix A contains an annotated bibliography, describing reference material specific to MTBE. Appendix B provides information regarding geographic participation in the Oxyfuels and RFG Programs, the MTBE content of representative reformulated petroleum fuels, and the current regulatory framework dealing with MTBE. Representative calculations used to evaluate the partitioning of MTBE between the dissolved and vapor phases are presented in Appendix C. Methods of chemical analyses of environmental samples, appropriate to sites suspected to be contaminated with MTBE, are discussed in Appendix D. Techniques that can be used to quantify biodegradation rates are described in Appendix E. A draft of this report was originally submitted to AFCEE for review and comment. Comments provided by the reviewer (Waste Policy Institute) are included in Appendix F, together with Parsons ES' responses.

SECTION 2

PROPERTIES AND ENVIRONMENTAL FATE OF MTBE

Methyl tertiary-butyl ether (methyl *tert*-butyl ether, or MTBE; also, 2-methoxy-2-methylpropane) is a volatile organic compound (VOC) that has been added to gasoline in many parts of the United States since 1979. This section describes the history of MTBE usage in the United States, and discusses some of the physical and chemical characteristics that influence its occurrence, movement, and fate in the environment.

2.1 HISTORY OF DEVELOPMENT AND USE OF METHYL *TERT*-BUTYL ETHER

MTBE was originally used as a replacement for tetraethyl lead in gasoline to enhance octane ratings in mid- to high-grade fuels, at concentrations of 2 percent to 8 percent by volume (USEPA, 1998a). As tetraethyl lead in gasoline was phased out in the early 1980s, the use of MTBE rapidly increased. From 1980 to 1986, the commercial production of MTBE increased at a rate of about 40 percent per year (Suflita and Mormile, 1993). Its use and production has continued to increase, and since 1993, MTBE has become the second most produced organic chemical in the United States (USEPA, 1998b), with 350 billion liters (92 billion gallons) of MTBE being produced in 1997 (Zogorski *et al.*, 1998).

In addition to being an octane enhancer, MTBE is the preferred of several gasoline oxygenates, including other ethers [di-isopropyl ether (DIPE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME)] and alcohols [ethanol and *tert*-butyl alcohol (TBA)]. The oxygen content of conventional gasoline ranges from 0.0 to 3.7 percent by weight, and averages less than 0.5 percent (Clean Fuels Development Coalition *et al.,*

1997), so under certain conditions fuel combustion is incomplete, and noxious emissions (primarily carbon monoxide and ozone) can be generated. Fuel containing oxygenates combusts more efficiently than un-oxygenated gasoline and thereby reduces emissions of carbon monoxide and ozone. In January 1988, Denver, Colorado became the first metropolitan area in the United States to voluntarily use oxygenated gasoline to reduce vehicle emissions in order to improve air quality. Denver's oxygenated gasoline program was implemented during the winter months to reduce carbon monoxide levels during cold weather.

In 1990, amendments to the Clean Air Act required areas in violation of the national ambient air quality standards to use oxygenated gasoline, and the USEPA initiated the Oxyfuels Program to meet this requirement. Metropolitan areas that did not meet standards for carbon monoxide were required to use oxygenated fuels beginning not later than November 1, 1992. The Oxyfuels Program requires the use of gasoline containing a minimum of 2.7 percent oxygen (by weight) during the fall and winter months. Currently, metropolitan areas in 14 states participate in the program; these are listed in Appendix B.

The USEPA's Reformulated Gasoline (RFG) Program was developed to address air-quality issues associated with ozone non-attainment areas; Phase I of the RFG Program went into effect beginning January 1, 1995, for the worst ozone non-attainment areas. . Phase I (and Phase II, scheduled to begin January 1, 2000) of the RFG Program require a minimum oxygen content in gasoline of 2.0 percent by weight. There are currently 10 US metropolitan areas required to use RFG year-round, including Philadelphia, Baltimore, New York, Hartford, Chicago, Milwaukee, Houston, San Diego, Sacramento, and Los Angeles. In addition, 22 other metropolitan areas have voluntarily entered the RFG Program, so that a total of 32 metropolitan areas in 17 states and the District of Columbia, are using RFG (Clean Fuels Development Coalition *et al.,* 1997). Areas participating in the RFG Program are listed in Appendix B.

Neither the RFG Program nor the Oxyfuels Program specifically requires the use of MTBE; however, MTBE is the most common oxygenate in reformulated fuels, used in about 80 percent of oxygenated fuels sold in the US. The second most common oxygenate (ethanol) is used in approximately 15 percent of oxygenated fuels. The remaining 5 percent of oxygenated gasoline is produced with TAME, TBE, DIPE, and TBA. MTBE currently is the preferred oxygenate because of its relatively lower cost (compared with ethanol). Furthermore, MTBE can be blended with gasoline without phase separation, and is therefore regarded as more compatible with gasoline than ethanol. This characteristic enables gasoline and MTBE to be blended at the refinery; the gasoline/MTBE mixture can then be distributed through existing pipeline networks. In contrast, ethanol must be shipped separately from gasoline and then blended at the distribution terminal shortly before use.

It is difficult to ascertain which areas of the US are using gasoline containing MTBE, or which oxygenate is added to gasoline in particular RFG or Oxyfuels Program areas; however, several general trends are apparent (USEPA, 1998b). MTBE is still used to increase octane levels in conventional gasoline, and can be found in gasolines not specifically blended as RFG or oxygenated, at concentrations less than 8 percent by weight (McCarthy and Teimann, 1998). The Oxyfuels Program requires the use of gasoline having a minimum content of 2.7 percent oxygen (by weight). This requirement can be met by using MTBE at a concentration of 15 percent (by volume) in gasoline, or by using ethanol at a concentration of 7.3 percent (by volume), and is typically met using ethanol. The oxygen content required by the RFG Program (2.0 percent by weight) can be achieved using MTBE at a concentration of 11 percent (by volume) in gasoline, or using ethanol at a concentration of 5.4 percent (by volume).

In some areas, MTBE may be used throughout the year, but because MTBE can reduce the tendency of volatile fuels to evaporate, it is substituted for ethanol more frequently in summer months. Furthermore, because of the complicated nature of fuel distribution systems, oxygenated gasoline may be distributed occasionally to locations near

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RFG/Oxyfuels areas, that do not participate in the RFG or Oxyfuels Programs. This is a situation that the petroleum industry tries to avoid, because oxygenated fuel is more expensive to produce than conventional gasoline (USEPA, 1998b). The results of a USEPA survey of oxygenate use in gasolines in RFG areas are presented in Appendix B.

2.2 SOURCES OF MTBE IN THE ENVIRONMENT

MTBE can be introduced to the environment from point sources (petroleum fuels leaking from storage tanks and pipelines, and fuel spills) and non-point sources. Most MTBE in soil and water is probably a result of fuel leaks or spills. Groundwater contamination by MTBE has been associated with gasoline, diesel fuel, jet fuel, heating oil, aviation fuel, and waste oil (Kostecki and Leonard, 1998). Non-point sources of MTBE in the environment include atmospheric distribution of MTBE in the vapor phase, and MTBE in precipitation.

2.2.1 MTBE in Air

Zogorski *et al.* (1997b) report that the median concentration of MTBE in the atmosphere in the United States is on the order of 1 part per billion by volume (ppb-v) or less. Because of its low Henry's Law constant, MTBE readily partitions from the atmosphere to precipitation, and the concentration of MTBE in precipitation is directly related to the atmospheric concentration of MTBE. Zogorski *et al*. (1997b) estimate that given a typical concentration of MTBE in ambient air (1 ppb-v), the concentration of MTBE in precipitation would be about 1 microgram per liter (g/L) at a temperature of 5 degrees Celsius (^{o}C) [41 degrees Farenheit (^{o}F)].

Higher concentrations of MTBE in air may occur in close proximity to service stations, highways, parking garages, and refineries, where MTBE is being introduced to the atmosphere. An MTBE concentration in air of 30 ppb-v (a possible atmospheric concentration near a source of MTBE) is estimated (Zogorski *et al*., 1997b) to produce MTBE concentrations as great as 30 g/L in precipitation, at the same temperature. Therefore, precipitation falling near sources of vapor-phase MTBE will probably contain

elevated concentrations of MTBE. Representative calculations used to estimate the partitioning of MTBE between the dissolved and vapor phases are presented in Appendix C.

If MTBE in precipitation migrates in the dissolved phase to the water table, increased levels of MTBE in nearby groundwater could result (Zogorski *et al.,*1997b). Pankow *et al.* (1997) report the results of a modeling study to evaluate the possibility that volatile chemicals in the atmosphere, including MTBE, could function as non-point sources of chemicals in groundwater. Five cases were examined to determine whether MTBE could migrate to the water table, at a depth of five meters below land surface, within the 10- to 15-year time frame that MTBE has been used in gasoline. It was concluded that MTBE could reach groundwater from non-point sources within 5 years for a situation in which there was net infiltration of 36 centimeters per year (cm/yr).

MTBE concentrations associated with point sources are typically in the range of 0.1 to 100 milligrams per liter (mg/L) (Davidson, 1995). Low concentrations (0.2 to 3 g/L) of MTBE in groundwater are most likely due to non-point sources (Squillace *et al.,* 1996).

2.2.2 MTBE in Ambient Groundwater

During 1993 and 1994, the U.S. Geological Survey (USGS) sampled a total of 759 wells in order to evaluate the natural and anthropogenic factors affecting the quality of ambient groundwater at shallow depth beneath urban and agricultural areas (Squillace *et al.,* 1996). In addition, 412 wells completed in deeper, regionally-extensive aquifers were sampled. This sampling event was part of the first phase of the National Water-Quality Assessment (NWQA) Program.

The 759 samples of groundwater collected at shallow depth were from urban and agricultural areas. Of the 210 urban wells and springs sampled, 27 percent contained MTBE at concentrations greater than the reporting limit of 0.2 g/L. Of the 60 VOCs analyzed, the frequency of detection of MTBE was second only to that of chloroform.

The maximum concentration of MTBE in groundwater samples from shallow depth in urban areas was 100 g/L. MTBE was found much less frequently in deeper groundwater from regional aquifers than in the shallow groundwater. Groundwater samples from four of 412 wells sampled (1 percent) contained detectable concentrations of MTBE; the maximum concentration of MTBE in groundwater samples from deeper aquifers was 1.3 g/L.

Additional wells were sampled in 1995, and the results of the study were reevaluated for a three-year sampling period (Zogorski *et al.,* 1998). All aquifers sampled were classified according to use as drinking-water sources, or non-drinking-water sources. MTBE was detected in 12 of 83 sampled wells (14 percent) in urban areas, and in 19 of 949 sampled wells (two percent) of drinking-water wells in rural areas. Concentrations of MTBE were similar to those found in 1993 and 1994.

The State of Maine also has sampled drinking-water supplies throughout the state to assess the occurrence of MTBE and BTEX compounds (State of Maine, 1998). Nine hundred fifty-one randomly selected private wells and other household water supplies (e.g., springs and lakes) and 793 public water supplies were sampled. Maine has been using reformulated gasoline (comprising 11 percent MTBE) since 1991, when the state joined the RFG program.

MTBE was detected in groundwater samples from domestic wells at a frequency of 15.8 percent, and was the most frequently detected fuel constituent, with toluene the second most frequently detected (2.1 percent). The concentrations of MTBE in groundwater samples from about 1 percent of the wells sampled exceeded the State of Maine's drinking-water standard for MTBE (35 g/L). Benzene, ethylbenzene, and xylene isomers were each detected in fewer than 1 percent of the samples. The detection frequency of MTBE in public water supplies was similar to that of private water supplies. Again, MTBE was the most frequently detected fuel constituent, occurring in 16 percent

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of public water supplies. None of the detections of MTBE in public water supplies exceeded the State drinking water standard.

2.3 REGULATORY STANDARDS FOR MTBE

In December 1997, the USEPA (1997a) issued a drinking-water advisory for MTBE of 20 to 40 g/L, to protect consumer acceptance of water resources and also to provide a large margin of safety from potential toxic effects resulting from exposure to MTBE. The drinking-water advisory is based on MTBE's low taste and odor threshold, and is five to six orders of magnitude lower than the concentrations associated with adverse health effects in laboratory animals. Shen *et al.* (1997) report an odor threshold concentration range of 13.5 to 45.4 g/L in tests conducted by the Orange County, California Water District. Zogorski *et al.* (1997b) report that at least 11 states have established, or are promulgating, drinking-water standards or health advisory guidelines for MTBE.

At the Federal level it appears unlikely that enforceable standards will be adopted soon (Happel *et al.*, 1998). The USEPA has currently designated MTBE as an unregulated chemical. The 1996 amendments to the Safe Drinking Water Act require that a list of unregulated contaminants be established (Drinking Water Contaminant Candidate List) in order to determine regulatory priorities. Compounds on this list are segregated as regulatory determination priorities, research priorities, and occurrence priorities. As of February 1998, MTBE was listed as a research priority and occurrence priority but not a regulatory determination priority. Specifically, USEPA's position is that there is a lack of information regarding health research, treatment research, and occurrence data that prevents the adoption of scientifically-based standards for MTBE. Of those compounds considered to be regulatory priorities, five or more will be selected for potential regulation by August 2001. If regulations are considered appropriate, they must be proposed by August 2003 and enacted by February 2005. Because MTBE is not currently a regulatory priority, it does not appear likely that standards would be enacted until after February 2005.

Updates to priority lists will be based on the National Drinking Water Contaminant Occurrence Database (NDWCO) and the Unregulated Contaminant Monitoring Regulations, both of which are to be completed in August 1999. Subsequent reviews of priority lists will occur every six years. The minimum period of time required between a contaminant being listed as a regulatory determination priority and action levels being established for that compound also is six years. Therefore, even if MTBE becomes listed as a regulatory determination priority at the next opportunity (2005), it is not likely to become a regulated contaminant until 2011, at the earliest. In the near future, states probably cannot expect USEPA's regulatory guidance other than the current suggested, but unenforceable, advisory level (20 - 40 g/L).

In the absence of Federal regulations, several of the states have adopted action-level concentrations, and/or cleanup concentrations for MTBE in soil and groundwater (Appendix B). Action-level concentrations for MTBE in groundwater range from "not detectable" (South Dakota) to "none established" (Arizona, Missouri, Vermont). The typical action-level concentrations range from 20 to about 200 g/L, similar to the advisory level established by the USEPA.

2.4 PHYSICAL AND CHEMICAL COMPOSITION OF FUEL HYDROCARBONS AND OXYGENATES

Petroleum fuels are distillates of crude petroleum comprising a complex mixture composed predominantly of paraffins, cycloparaffins and aromatic groups, together with other constituents added as octane enhancers, oxygenates, or to improve the evaporation and condensation characteristics of the fuel. The BTEX compounds are primary constituents of petroleum-distillate fuels, and are chemicals of environmental concern in fuels because they are relatively soluble and toxic, and can be mobile in the environment (California Department of Health Services, 1988). As previously described, MTBE is a fuel oxygenate, added to many gasoline blends to reduce emissions or as an octane enhancer.

2.4.1 Chemical Structure of Hydrocarbon Compounds

Nearly all organic chemicals are products or byproducts of the refining and processing of crude petroleum. Petroleum hydrocarbon compounds are composed of carbon and hydrogen atoms, arranged into an almost infinite number of discrete molecules. On the basis of their structure, these molecules are classified as alkanes, alkenes, and aromatic hydrocarbons.

Alkanes, or paraffins, are the major constituents of crude oil and usually the major constituents of refined petroleum products. Alkenes, or olefins, are not usually constituents of crude oil, but are formed during the refining process. Alkanes and alkenes are virtually non-toxic, and most are nearly insoluble in water (Zemo *et al.*, 1995).

Aromatic hydrocarbon compounds are based on the benzene ring structure, with conjugated carbon-carbon double bonds, which imparts some unique properties. The monoaromatic compounds (benzene, toluene, ethylbenzene, xylene isomers, and substituted benzenes) are relatively soluble in water, as compared with alkanes and alkenes. Their relatively greater solubility causes aromatic compounds to be quite mobile in the environment. Polycyclic aromatic hydrocarbon compounds (PAHs) contain two or more benzene-ring structures (e.g., napthalene and acenaphthene), and range from moderately soluble to virtually insoluble in water. Aromatic hydrocarbon compounds are the most toxic constituents of petroleum products (Zemo *et al.*, 1995).

2.4.1.1 Composition of Petroleum-Based Fuels

Gasoline is a mixture, consisting almost exclusively of hydrocarbons in the boiling-point range between 0 C and 200 C, while diesel fuel, kerosene and fuel oil consist of hydrocarbons in the boiling-point range between 175 C and 325 C (Nyer and Skladany, 1989). There are several hundred different hydrocarbons, in varying proportions, in any given petroleum-based fuel (Neff *et al.*, 1994), but most of these constituents are relatively inert, and are readily degraded (Lyman *et al.*, 1990). The composition and structure of

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particular classes of hydrocarbon compounds greatly influence their chemical properties, which, in turn, affect their mobility and fate in the environment.

The class of saturated hydrocarbon compounds, including the normal alkanes, comprise about 60 to 75 percent of the mass of a typical petroleum fuel (Griest *et al.*, 1985; Heath *et al.*, 1993; Neff *et al.*, 1994). The BTEX constituents may comprise up to 30 weight percent of a typical gasoline, but occur at relatively low concentrations in mid-distillate-range fuels (Heath *et al.*, 1993; Neff *et al.*, 1994). Certain polycyclic aromatic hydrocarbons may also be present in higher-boiling-range fuels (Griest *et al.*, 1985).

The number of carbon atoms present in a hydrocarbon compound, and the molecular structure of the compound, have a major effect on its properties. In general, the aqueous solubility of a compound rapidly decreases as the number of carbon atoms in the compound increases; vapor pressures also decrease as carbon numbers increase. High vapor pressures indicate that a compound is readily volatilized from the pure chemical phase, or from a chemical mixture; low vapor pressures are associated with chemicals that are semi-volatile or non-volatile. For all classes of hydrocarbons, aqueous solubility decreases, and the tendency of the hydrocarbon compound to sorb to soil particles (or "partition" to soil), increases as the number of carbon atoms and compound molecular weight increase (Neff *et al.*, 1994). As a general rule, hydrocarbon compounds with an aqueous solubility less than about 0.1 mg/L will have limited mobility in soils, and are unlikely to migrate to groundwater.

2.4.1.2 MTBE, TBA, and TBF

MTBE is a volatile, flammable, colorless liquid having a distinctive "terpene-like" odor (ARCO, 1988). It is a polar molecule with chemical formula $C_5H_{12}O$ and the chemical structure of a methoxyl ether (Figure 2.1).

MTBE is usually synthesized from two relatively inexpensive reactants, methanol and isobutylene. Methanol is commonly generated from natural gas, and isobutylene can be

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derived from petroleum in the refining process (Fité, 1997). ARCO Chemical Company (1988) (now Lyondell), the largest producer of MTBE, reports that refined MTBE typically has a purity of 97.5 percent. Impurities (on a percent weight basis) include di-isobutylene, tri-isobutylene and *tert*-butyl alcohol (TBA) (0.6 percent combined), methanol (0.2 percent), C_4 hydrocarbons (1.0 percent), C_5 hydrocarbons (0.4 percent), other hydrocarbons (0.3 percent), and water (<0.05 percent).

The ethers (including MTBE), alcohols (including TBA), and formates (including *tert*-butyl formate (TBF) all contain oxygen, but the oxygen atom in ethers and alcohols is singly-bonded, while all formates contain an oxygen atom double-bonded to a carbonyl carbon, in addition to another oxygen single-bonded to the carbonyl carbon atom. The attached oxygen atom imparts a higher degree of polarity to this class of compounds. As a consequence of the greater polarity of their molecular structure, ethers, alcohols and formates tend to be more soluble in water than hydrocarbon compounds composed of only carbon and hydrogen.

The general physical and chemical characteristics governing the movement and fate of MTBE in various environmental media are discussed in the following sections.

MTBE
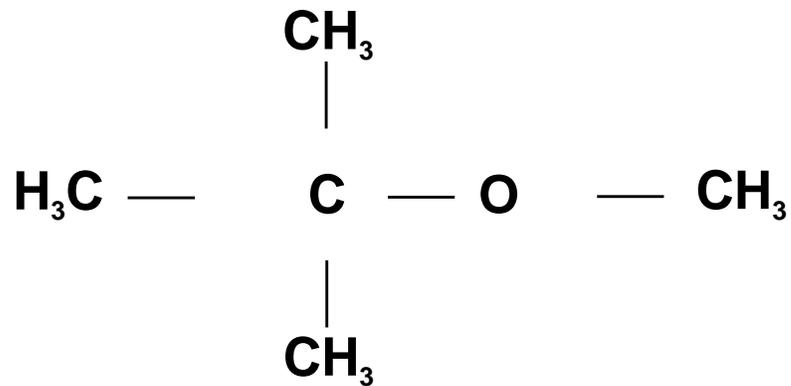
$$CH_3$$
$$|$$
$$H_3C — C — O — CH_3$$
$$|$$
$$CH_3$$

2.5 PHASE PARTITIONING OF CHEMICALS IN THE ENVIRONMENT

Several processes control the movement of chemicals through soils as non-aqueous phase liquids (NAPLs or fuels), solutes, compounds sorbed to the aquifer matrix, and gases. Petroleum hydrocarbons are usually released into the subsurface as NAPLs. Once a petroleum fuel has been introduced into the environment, it interacts with the surrounding soils. The primary processes affecting fuel constituents in the subsurface include dissolution, advection, dispersion, sorption, volatilization, and chemical and biological degradation.

Depending upon particular conditions, chemicals can exist in the environment in any of four different phase:

- In the liquid phase as either a pure compound or in a chemical mixture (e.g., fuels);

- In the aqueous phase (dissolved in water);

- Sorbed to soil particles; or

- In the gaseous (vapor) phase.

The degree to which a particular chemical is segregated among these phases is known as *partitioning*. Two basic types of partitioning are significant when evaluating the fate and transport of most chemical compounds. The first is partitioning of a single compound from a pure chemical or chemical mixture into air and/or water (e.g., partitioning of BTEX constituents from free-phase gasoline at a spill site). After moving out of the pure chemical or chemical mixture, compounds dissolved in water or present in the vapor phase will partition among the three phases in the subsurface environment, becoming dissolved in water, sorbed to soil, or volatilized in soil gas. The partitioning of a particular compound among the phases, and its subsequent migration and fate in the environment, depends on its chemical properties (Jury *et al*., 1983), including:

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- chemical volatility (related to the chemical's vapor pressure);

- chemical air-gas diffusion coefficient (related to the chemical's volatility);

- solubility of the compound in water;

- chemical water-liquid diffusion coefficient (related to the chemical's solubility);

- chemical organic-carbon partition coefficient;

- Henry's Law constant for the chemical; and

- rate of chemical decay via biotic and abiotic mechanisms.

Subsurface transport of fuel constituents as NAPL, in the dissolved-phase, or in the vapor-phase, like movement of any liquid in the subsurface, is driven by potential gradients – gravitational, hydraulic, or chemical. In the unsaturated zone, gravitational and hydraulic potential gradients are primarily vertical, so that the direction of movement is generally downward. In general, NAPLs will migrate through the soil in the unsaturated zone until they reach the water table (Figure 2.2). At that point, the various constituents of the NAPL begin to dissolve in groundwater, in accordance with their relative solubilities (Mallon, 1989).

The density of most refined petroleum products is less than the density of water, and the solubilities of most of the constituents of refined petroleum products are relatively low (Neff *et al*., 1994). As a consequence, the bulk of a petroleum NAPL will not dissolve into groundwater, and cannot migrate as a NAPL below the water table. Rather, a petroleum fuel that migrates to the water table will generally spread laterally from the initial point of introduction as an immiscible phase at the air-water interface.

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Underground Storage Tanks

Liquid-Phase Hydrocarbon

Plume of Dissolved Hydrocarbon

10,000 ppb

1,000 ppb

100 ppb

10 ppb

No Detection

Service Station

Leaky Tank

Liquid-Phase Hydrocarbon

Smear Zone

Sand

Groundwater Flow

10,000 ppb

1,000 ppb

100 ppb

10 ppb

No Detection

Clay
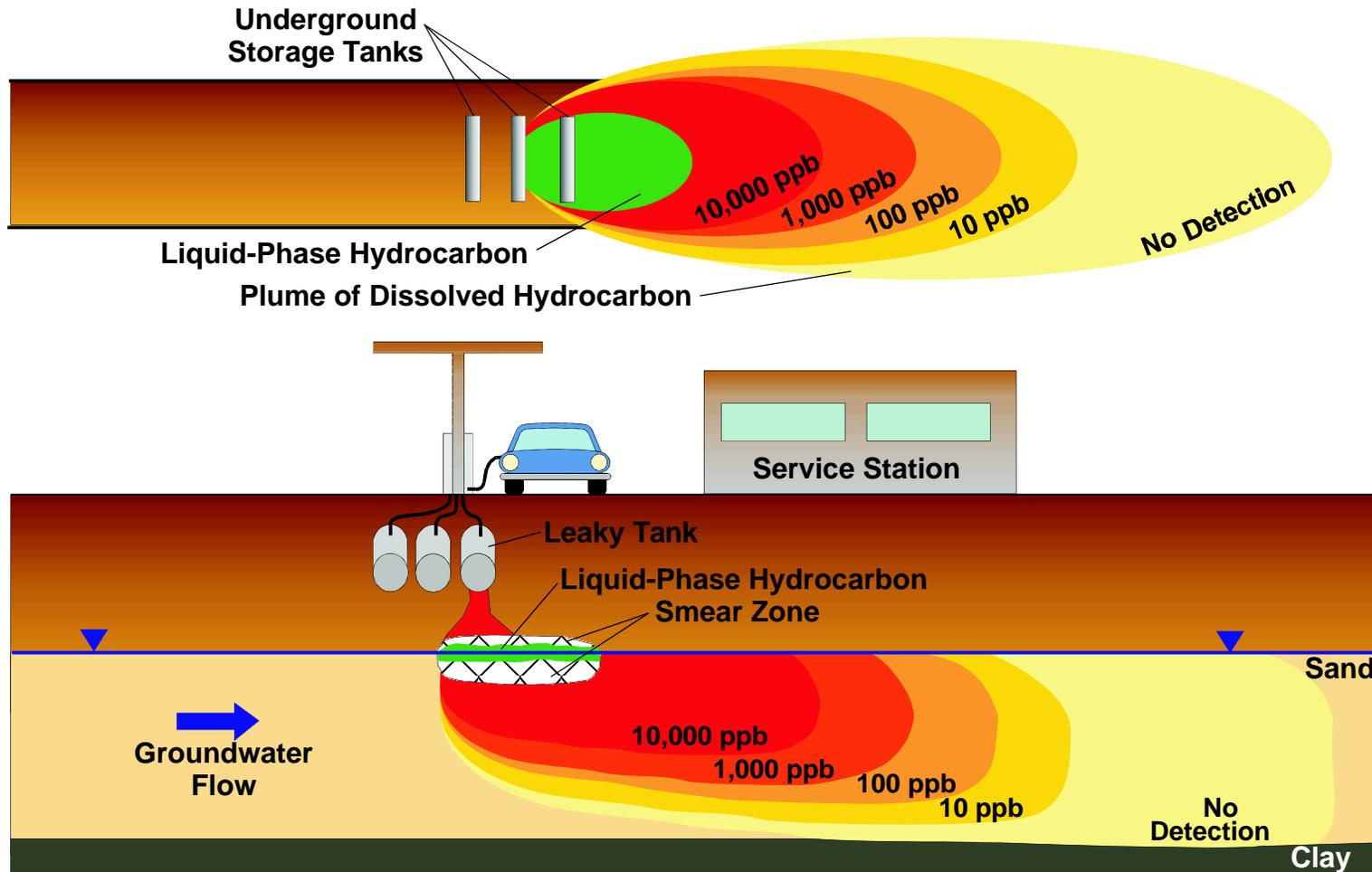
FIGURE 2.2

UST LEAK AND DISSOLVED HYDROCARBON PLUME

MTBE Technical Summary Report

Parsons

parsons engineering science, inc.

Denver, Colorado

Seasonal or other fluctuations in the elevation of the water table can result in residual petroleum NAPL being trapped below the water table, producing a "smear zone" of residual petroleum product in direct contact with groundwater (Figure 2.2). Because the more-soluble constituents of the petroleum NAPL gradually dissolve from the NAPL, at and below the water table, into groundwater, the "smear zone" can continuously contribute constituents from the fuel to the dissolved phase, thereby functioning for some extended period of time as a source of contaminants in groundwater.

After fuel constituents have been dissolved in water, aqueous-phase transport can occur in the unsaturated and the saturated zones. Dissolved fuel constituents can enter the unsaturated zone via infiltration of water which already contains constituents dissolved from an above-ground source, or the constituents can become dissolved as percolating water passes over and through petroleum product in soil. As water percolates through the unsaturated zone, fuel constituents present as bulk liquid, a sorbed phase, or a vapor phase, can be dissolved and migrate with the infiltrating water to the water table. Dissolved constituents are carried downward in percolating water ("advective transport"). Volatile compounds move in response to concentration gradients between soil moisture and air-filled pore spaces ("diffusive transport"); and subsequent vapor-phase migration is driven by concentration gradient within air-filled pores, so that chemicals in the vapor-phase generally move from the subsurface to the atmosphere (Mallon, 1989).

The transport of dissolved fuel constituents in the unsaturated zone depends primarily on the permeability of the soil, its water content, and the concentrations of dissolved chemicals in percolating water. The transport of volatilized fuel constituents in the unsaturated zone depends primarily on the permeability of the soil, its water content, and the ambient air temperature and barometric pressure. Below the water table, there are no continuous air-filled pores, and vapor-phase transport does not occur.

The primary mechanism by which dissolved constituents migrate in the saturated zone is advective transport (Figure 2.2 and Section 2.6.2). The direction and rate of advective transport are controlled primarily by the hydraulic conductivity and effective porosity of

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the aquifer matrix, and local hydraulic gradients (Neff *et al.*, 1994; Reilly *et al.*, 1987; USEPA, 1989).

2.6 PHYSICAL AND CHEMICAL TRANSPORT AND ATTENUATION MECHANISMS AFFECTING MTBE

The principal physical and chemical mechanisms governing the migration of contaminants in the subsurface include dissolution, advection, dispersion, sorption, and volatilization. These mechanisms are discussed in the following sections. Consideration of the chemical properties that affect the migration of chemicals in the physical environment can assist in predicting how chemicals will interact with environmental media, and how particular conditions might influence the fate of MTBE in the environment. Representative chemical properties for the BTEX constituents, MTBE, and other fuel oxygenates are summarized in Table 2.1. Note that literature values for a particular chemical property, as reported by different investigators, can vary widely. The values listed in Table 2.1 are judged to be most representative of, or in the median range of values reported for a particular chemical.

2.6.1 Solubility and Dissolution

The aqueous solubility of a chemical species provides an indication of how readily it will dissolve into and migrate with groundwater. Ethers and alcohols are highly soluble in water, with aqueous solubilities reportedly ranging from about 40,000 to 50,000 mg/L at 25°C for MTBE to completely miscible at 25°C (Zogorski *et al*., 1997b) for TBA (Table 2.1). As a consequence of their molecular structure, the monoaromatic hydrocarbons are only moderately soluble. In contrast, other fuel constituents (longer-chained alkanes and PAHs) are nearly insoluble in water, with reported values for

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Compound	Molecular Weight (g/mol) [b]	Henry's Law Constant (atm-m^3/mol) [c]	Vapor Pressure (mm Hg @ 20°C) [d]	Density (g/cm^3) [e]	Solubility (mg/L) [f]	K_{oc} [a] (mL/g) [g]	Log K_{oc}	Typical First-Order Degradation Rate Constant in Water (day^{-1})
Benzene	78.11 [h]	5.43E-03 [i]	76 [j]	0.877 [h]	1,780 [j]	91.2 [i]	1.96	0.001 [k]
Toluene	92.14 [h]	5.94E-03 [i]	22 [j]	0.867 [h]	515 [j]	151 [l]	2.18	0.001 [k]
Ethylbenzene	106.17 [h]	8.44E-03 [i]	7 [j]	0.867 [h]	152 [j]	257 [l]	2.41	0.001 [k]
o-Xylene	106.17 [h]	5.10E-03 [i]	5 [j]	0.880 [h]	175 [j]	129 [l]	2.11	0.002 [k]
m-Xylene	106.17 [h]	7.68E-03 [i]	6 [j]	0.864 [h]	146 [j]	159 [l]	2.20	0.01 [k]
p-Xylene	106.17 [h]	7.68E-03 [i]	6.5 [j]	0.861 [h]	198 [j]	204 [l]	2.31	0.01 [k]
1,2,4-Trimethylbenzene (1,2-4-TMB)	120.19 [h]	5.70E-03 [l]	2.03 [l]	0.862 [h]	52 [o]	772 [p]	2.89	0.001 [k]
MTBE	88.15 [n]	5.87E-04 - 3E-03 [n]	245-256 [n]	0.7405 [n]	43,000 - 54,300 [n]	10.84 - 12.33 [n]	1.035 - 1.091	0.0000 - 0.001
tert-Butyl Alcohol (TBA)	74.12 [h]	1.04E-05 - 1.47E-05 [n]	40-42 @25°C [n]	0.791 [n]	miscible [n]	37.2 [n]	1.57	N/A [q]
tert-Butyl Formate (TBF)	102.13 [h]	2.72E-04 [n]	81 [n]	0.886 [n]	~40,000 [n]	12.9 [n]	1.11	N/A

[a] K_{oc} = organic carbon partition coefficient

[b] g/mol = grams per mole

[c] atm-m^3/mol = atmosphere-cubic meters per mole

[d] mm Hg@20°C = millimeters of mercury at 20 degrees Celsius

[e] g/cm^3 = grams per cubic centimeter

[f] mg/L = millgrams per liter

[g] mL/g = milliliters per gram

[h] Weast *et al.,* (1989)

[i] Howard *et al.,* (1990b)

[j] Verschueren, (1983)

[k] Howard *et al.*, (1991)

[l] Montgomery and Welkom, (1990)

[m] Howard et al., (1990a)

[n] Zogorski *et al.,* (1997)

[o] Neff *et al.,* (1994)

[p] AFCEE, (1995)

[q] Not Available

aqueous solubility ranging from 0.3 µg/L at 25°C for benzo(ghi)perylene (Verschueren, 1983) to 2,800 µg/L at 25°C for naphthalene (API, 1994).

Constituents having moderate to high solubilities typically are potentially the most mobile in the subsurface because they are most likely to be available for transport in the aqueous phase. The less-soluble chemicals typically become adsorbed or occluded in soil, and are unlikely to migrate appreciable distances in the aqueous phase. The solubility of neat MTBE (about 50,000 mg/L) is more than one order of magnitude greater than that of benzene (1,780 mg/L; Table 2.1). The partitioning of MTBE and benzene between an oil mixture (gasoline) and water is affected in part by the solubility of the two compounds in water. At a particular temperature, the solubility of a pure organic liquid is a constant (e.g., the values reported for solubility in Table 2.1). However, the solubility of a compound is reduced when other organic compounds are present in the liquid organic phase (e.g., gasoline). The result is that the equilibrium aqueous solubility of component species dissolving from a mixture will be:

$$S_i^e = \gamma_i \cdot X_i \cdot S_i^w$$

(2-1)

where:

S_i^e = effective solubility of component i (mass/volume);

γ_i = activity coefficient of species i in a mixture (usually very close to 1.0);

X_i = mole fraction of component i in the mixture (mole/mole); and

S_i^w = pure-phase aqueous solubility of component i (mass/volume).

For a compound having a molecular weight similar to the mean molecular weight of the mixture [~100 grams per mole (g/mol) for gasoline], X_i is closely approximated by the

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compositional fraction of the component on a weight or volume basis (Squillace *et al*., 1997).

The high aqueous solubility of MTBE, together with its high concentrations in oxygenated gasoline, can produce elevated concentrations of MTBE in water contaminated by gasoline spills. For a gasoline that is 10 percent by weight MTBE, X_i for MTBE will be about 0.1. Assuming no depletion of the MTBE in the gasoline resulting from dissolution into water, and a pure-phase aqueous solubility of 50,000 mg/L, the concentration of MTBE in water in contact with gasoline could be as high as 5,000 mg/L. For comparison, the maximum concentration of benzene in water in contact with gasoline might be about 50 mg/L (assuming benzene comprises 3 percent of a gasoline by weight [California Department of Health Services, 1988]), and the total aqueous solubility of all hydrocarbons in a non-oxygenated gasoline is generally about 120 mg/L (Poulsen *et al*., 1992).

Elevated concentrations of MTBE detected in groundwater near UST spill sites are consistent with calculated gasoline/water partitioning (Squillace *et al*., 1997). MTBE concentrations in the hundreds of mg/L have been reported for groundwater samples (Davidson, 1995; Buxton *et al*., 1997). These concentrations are not as high (thousands of mg/L) as might be expected for water in equilibrium with oxygenated gasoline. However, as water moves through and away from the source area, relatively uncontaminated groundwater will dilute the dissolved constituents to concentrations below gasoline/water equilibrium concentrations.

Furthermore, although the above calculation assumes that MTBE is not depleted, in reality, a gasoline spill will become depleted in MTBE, and all other soluble or degradable fuel constituents over time, so that as the fuel ages in the environment, the concentrations of fuel constituents partitioning into the dissolved phase will also decrease. This observation implies that the concentrations of fuel constituents, including MTBE, in groundwater near a spill may well be lower than the concentrations of fuel constituents at

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some distance downgradient from the spill, as a consequence of the changing composition of the fuel mixture through time.

The high effective solubility of MTBE during dissolution from the gasoline phase means that MTBE will partition out of gasoline and into the aqueous phase more readily than will other fuel constituents (Squillace *et al.*, 1996; ibid., 1997; ibid., 1998). The relatively lower effective solubilities of BTEX compounds indicates that a residual gasoline in soil can function as a continuing source, contributing BTEX contaminants to groundwater for long periods of time. By contrast, because of its partitioning characteristics, MTBE in residual fuel sources is depleted more rapidly than other fuel constituents. Thus, the contribution of MTBE from a fuel spill to groundwater may decrease markedly over time as the fuel becomes depleted in MTBE, although movement of BTEX and other constituents from the fuel spill to the aqueous phase may continue. For example, using Equation 2-1, and assuming a relatively low rate of groundwater movement through a typical fuel spill containing 10 percent MTBE and 3 percent benzene by weight, nearly 85 percent of the initial mass of benzene will remain in the fuel mixture, after a period of time sufficient to remove all of the MTBE from the fuel.

2.6.2 Advective Transport

After a chemical has been dissolved in vadose-zone water or groundwater, it migrates in the aqueous phase through the unsaturated and saturated zones under the influence of local hydraulic gradients. The physical laws that govern fluid motion are such that water tends to move from areas of relatively higher hydraulic potential ("head") to areas of relatively lower hydraulic potential. The path along which water moves from a region of greater hydraulic potential to a region of lower hydraulic potential is known as a *flowpath*, and the change in hydraulic potential along that flowpath is known as a *hydraulic gradient.* Movement of groundwater in a flow system therefore occurs from *upgradient* areas to *downgradient* areas.

Advective transport refers to the transport of solutes by the bulk movement of groundwater. Advection is the most important process driving the downgradient migration

of dissolved contaminants in the saturated subsurface. The seepage velocity of groundwater and dissolved chemicals moving via advective transport mechanisms alone is given by:

$$v_x = -\frac{K}{n_e}\frac{dh}{dL}$$ (2-2)

where: v_x = seepage velocity [L/T]

K = saturated hydraulic conductivity [L/T]

n_e = effective porosity [L^3/L^3]

dh/dL = hydraulic gradient [L/L]

In the absence of other effects (e.g., sorption), the migration velocity of the center of mass of a dissolved chemical slug is the average groundwater flow velocity. As will be described (Section 2.6.4), in most hydrogeologic regimes, the migration velocity of MTBE is approximately equal to the velocity of advective groundwater flow. Therefore, the seepage velocity of groundwater can be used to estimate the maximum downgradient extent of an MTBE plume, and must be considered when determining the relative importance of attenuation mechanisms.

2.6.3 Dispersion

As a solute moves away from the source it is affected by dispersive processes, including mechanical mixing of the dissolved chemical and molecular diffusion. Mechanical mixing occurs because each molecule of dissolved chemical follows a slightly different flowpath through the pore spaces within the porous medium; each also moves at a slightly different velocity. As an aqueous-phase contaminant moves through the subsurface it tends to mix with more "pristine" groundwater, thereby becoming diluted. Molecular diffusion, occurring in the presence of a chemical concentration gradient, causes dissolved-phase chemical to migrate from areas of relatively higher concentration to areas of relatively

lower concentration. Because molecular diffusion operates on a microscopic scale, and because diffusive velocities are generally much lower than the advective transport velocity of dissolved-phase chemical, the effects of mechanical mixing are generally much greater than the effects of chemical diffusion.

The net effect of dispersive processes acting on the dissolved chemical as it migrates through a porous medium is that the mass of chemical becomes distributed through an ever-increasing volume of earth material. This results in a decrease in chemical concentration with increasing distance downgradient from the chemical source. Because of its low soil sorption coefficient and relative biological recalcitrance, many investigators regard dispersion during advective transport as the most significant attenuation mechanism for MTBE in the environment (Happel *et al*., 1998). However, because dispersive processes do not actually remove chemical mass, decreases in chemical concentrations resulting from dispersion are associated with an increase in the volume of contaminated groundwater. For a more detailed discussion of dispersion, the reader is referred to the AFCEE Technical Protocol (1995).

2.6.4 Solid/Liquid Partitioning and Retardation

The rate of migration of a chemical in the subsurface also depends on the tendency of that chemical to partition between the dissolved and solid phases. Partitioning of a chemical between the dissolved phase and solid phase is commonly referred to as *soil adsorption* ("sorption"), and is quantified by the soil partition coefficient or distribution coefficient (K_d), which is the proportionality constant relating the amount of chemical sorbed to soil and the concentration at equilibrium in soil water (McCall *et al*., 1983):

$$C_{sorbed} = K_d \text{ X } C_{dissolved} \tag{2-3}$$

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where

C_{sorbed} = Concentration of chemical sorbed to soil [M/L^3];

K_d = Soil partition coefficient [L^3/M]; and

$C_{dissolved}$ = Concentration of chemical in adjacent soil water, at equilibrium with sorbed phase in soil [M/L^3].

This description of the process assumes that partitioning between the sorbed and dissolved phases is completely reversible, and that the equilibrium isotherm relating the relative concentrations in the two phases is linear (Neff *et al.*, 1994; Lyman *et al.*, 1990).

Soils are often extremely heterogeneous mixtures of different particle types, composition, and sizes. Because of this heterogeneity, the partition coefficient for a particular chemical is usually regarded as a site-specific property, and is likely to vary substantially with location, depending on the chemical composition and grain-size distribution of the soil used for determination of the partition coefficient. However, sorption studies on a wide variety of nonpolar organic compounds and soil and sediment types indicate that organic matter in soil controls sorption where there is sufficient organic matter present (more than about 0.1 percent organic carbon). This observation has been used as the basis for normalizing the linear partition coefficient to the concentration of total organic carbon in the soil (Karickhoff *et al.*, 1979; Karickhoff, 1981). The normalized partition coefficient for a particular chemical (K_{oc}) is calculated from the results of sorption studies, using

$$K_{oc} = \frac{K_d}{f_{oc}}$$
(2-4)

where

K_{oc} = Organic carbon partition coefficient [L^3/M]; and

f_{oc} = Fraction of organic carbon in the soil [ ].

If the organic carbon content of a particular soil is known or can be estimated, the fraction of organic carbon can be used, together with published values of organic carbon partition coefficients (Table B.1) to evaluate chemical partitioning, using

$$K_d = f_{oc} \text{ X } K_{oc} \tag{2-5}$$

All hydrocarbon compounds, and most other chemicals, sorb to soil to a greater or lesser degree; the fraction of sorbed hydrocarbons increases as the concentration of organic carbon in the soil increases. Partitioning to the solid phase tends to remove a solute from the aqueous phase, effectively slowing the rate of chemical migration. Chemicals having larger values of partition coefficients will be more strongly adsorbed to soil, and less mobile in the environment (Nyer and Skladany, 1989). Most fuel constituents, with the exception of MTBE, have relatively large partition coefficient values (Table 2.2), are strongly sorbed to soil particles, and travel only slowly in the dissolved (aqueous) phase. This phenomenon is known as *retardation*; and the ratio of the velocity of the retarded chemical to the local seepage velocity of groundwater is known as the *coefficient of retardation* (R):

$$R \quad = \quad \frac{V_{groundwater}}{V_{chemical}} \quad = \quad 1 + \left[\left(\frac{\rho}{n_e} \right) \times K_d \right] \tag{2-6}$$

where

$V_{groundwater}$ = average groundwater flow velocity [L/T],

$V_{chemical}$ = average velocity of center of mass of dissolved chemical slug [L/T],

ρ = unit weight of porous medium [M/L^3], and

n_e = effective porosity of the medium [L^3/L^3].

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TABLE 2.2
CALCULATION OF RETARDATION COEFFICIENTS
MTBE TECHNICAL SUMMARY REPORT

Compound	K_{oc}[a] (L/kg)	Maximum Fraction Organic Carbon[b]	Minimum Fraction Organic Carbon[b]	Distribution Coefficient K_d (L/kg) Maximum[c1]	Minimum[c2]	Bulk Density[b] (g/cm³)	Effective Porosity[b]	Coefficient of Retardation, R Maximum	Minimum	Ratio of Transport Velocity to Groundwater Velocity[d] Maximum	Minimum
Benzene	91.2	0.01	0.0001	0.912	0.009	1.76	0.25	7.42	1.06	0.13	0.94
Toluene	151	0.01	0.0001	1.510	0.015	1.76	0.25	11.63	1.11	0.09	0.90
Ethylbenzene	257	0.01	0.0001	2.570	0.026	1.76	0.25	19.09	1.18	0.05	0.85
o-Xylene	129	0.01	0.0001	1.290	0.013	1.76	0.25	10.08	1.09	0.10	0.92
m-Xylene	159	0.01	0.0001	1.585	0.016	1.76	0.25	12.16	1.11	0.08	0.90
p-Xylene	204	0.01	0.0001	2.040	0.020	1.76	0.25	15.36	1.14	0.07	0.87
1,2,3-TMB[e]	884	0.01	0.0001	8.840	0.088	1.76	0.25	63.23	1.62	0.02	0.62
1,2,4-TMB	772	0.01	0.0001	7.720	0.077	1.76	0.25	55.35	1.54	0.02	0.65
1,3,5-TMB	676	0.01	0.0001	6.760	0.068	1.76	0.25	48.59	1.48	0.02	0.68
MTBE	10.84	0.01	0.0001	0.108	0.001	1.76	0.25	1.76	1.01	0.57	0.99
	12.33	0.01	0.0001	0.123	0.001	1.76	0.25	1.87	1.01	0.54	0.99
Tert-Butyl Alcohol (TBA)	37.2	0.01	0.0001	0.372	0.004	1.76	0.25	3.62	1.03	0.28	0.97

[a] From Table 2.1; AFCEE, 1995; Knox *et al*., 1993; Montgomery *et al*., 1990; Zogorski *et al.*, 1997; and Abdul *et al*., 1989.

[b] Assumed value.

[c1] K_d = (Maximum Fraction Organic Carbon) x K_{oc}, units = liters per kilogram.

[c2] K_d = (Minimum Fraction Organic Carbon) x K_{oc}, units = liters per kilogram.

[d] = 1/R.

[e] TMB = trimethylbenzene.

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The processes of sorption and retardation, acting on fuel hydrocarbons, are discussed in detail in the AFCEE Technical Protocol (1995).

As is evident from Equation 2-5, the degree of sorption and retardation are related to the distribution coefficient of a compound and the organic carbon content of the aquifer. Because of its affinity for the aqueous phase (low distribution coefficient), the retardation of MTBE is minimal is most groundwater systems. For example, assuming a typical organic carbon fraction of 0.01 percent (Table 2.2), the coefficient of retardation estimated for MTBE is approximately one, indicating that under many circumstances MTBE will move at a velocity very close to that of the advective groundwater flow velocity (MTBE is a "conservative" constituent). By contrast, the BTEX constituents will probably move in the aqueous phase at some fraction of the groundwater flow velocity. The differences in migration velocities between MTBE and BTEX constituents are even more pronounced in porous media containing greater proportions of organic carbon. If the organic carbon content is 1 percent (Table 2.2), MTBE will move at a velocity approximately one-half the advective groundwater flow velocity, while BTEX constituents will migrate at velocities ranging from about one-tenth to one-twentieth the advective groundwater flow velocity. The substantial differences in flow velocities among MTBE and BTEX compounds indicates that if these substances are introduced to groundwater at approximately the same time, the MTBE and BTEX plumes will separate with increasing migration distance from a fuel spill, as MTBE migrates more rapidly downgradient.

These predictions are verified by the results of large-scale surveys of MTBE behavior in the subsurface (Buscheck *et al*., 1998; Happel *et al.,* 1998; Mace and Choi, 1998; Rong, 1998) and by individual case studies (Weaver *et al*., 1996). In general, because MTBE is more mobile than the BTEX compounds, MTBE plumes can be more extensive than associated BTEX plumes, and may affect groundwater at greater distances from gasoline spills than will BTEX. Furthermore, with increasing time in the subsurface, MTBE plumes and BTEX plumes have been observed to gradually dissociate, because of

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the disparity in migration velocities (Happel *et al.,* 1998). At a site on Long Island, MTBE migrated a distance of nearly 6,000 feet from leaking gasoline underground storage tanks – more than 1,000 feet further than detectable concentrations of benzene. Although the benzene plume was nearly continuous from its source to maximum downgradient extent, the MTBE plume was only generally associated with the benzene plume, and had detached from the source. MTBE had been rapidly depleted from the gasoline phase in the source area as a consequence of preferential partitioning from the fuel source to the aqueous phase.

2.6.5 Volatilization

Volatilization is the process by which a constituent partitions from a solid or liquid phase to the gaseous (vapor) phase. The volatility of a particular chemical is a function its vapor pressure and Henry's Law Constant. The vapor pressure of a substance at a reference temperature is the pressure exerted by the vapor phase of the substance in equilibrium with the liquid or solid phase of the substance. A chemical with a high vapor pressure has a greater tendency to volatilize than does a chemical with a low vapor pressure. The Henry's Law constant is a measure of the relative tendency of a chemical to move between the aqueous and vapor phases, and is a function of the vapor pressure and solubility of the chemical. A chemical with a high Henry's Law constant will have a high ratio of chemical concentration in the vapor phase compared with that chemical's concentration in the dissolved phase, and again will be more likely to volatilize to the surrounding atmosphere. A compound having a Henry's Law constant greater than about 0.001 atm-m^3/mol (at standard temperature and pressure) will readily volatilize from water (Lyman *et al.*, 1990). Included in this category are the BTEX compounds (Table 2.1), alkanes up through dodecane, and aromatic and substituted aromatic compounds through naphthalene (Neff *et al.*, 1994). However, the range of Henry's Law constants reported for MTBE, TBA, and TBF is one to two orders of magnitude lower than the Henry's Law constants for BTEX compounds, indicating that potential for transfer of oxygenates to the atmosphere through volatilization is limited. The relatively lower values of Henry's Law

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constants for oxygenates also explain why MTBE and TBA can be somewhat difficult to remove from water by aeration (Squillace *et al*., 1997).

2.7 BIODEGRADATION OF MTBE

2.7.1 Overview of Biodegradation Processes

Nearly all soils contain colonies of bacteria and fungi that are capable of biodegrading at least some hydrocarbon compounds. Soil bacteria and fungi are tremendously diverse, and readily adapt to utilizing different types of organic molecules as their sole or supplemental carbon source (Scow, 1990). Many genera of microorganisms are able to completely oxidize alkanes, and to a lesser extent, aromatic hydrocarbons and heterocyclic compounds, to carbon dioxide and water. Although all organic compounds found in petroleum-based fuels can be degraded by bacteria under oxic conditions (Dragun, 1988), the rates of hydrocarbon degradation for some compounds can be much lower to nonexistent under anoxic conditions. Following the release of a petroleum hydrocarbon to soil, different hydrocarbon classes are degraded simultaneously, but at varying rates, by indigenous microbiota. Normal alkanes of low molecular weight (C-8 to C-22) are metabolized most rapidly, followed by isoalkanes and higher-molecular-weight normal alkanes, olefins, monoaromatic compounds (benzenes), and PAH compounds (Howard *et al.*, 1991; Neff *et al.*, 1994; Park *et al*., 1990).

During biodegradation, microorganisms transform available nutrients into forms useful for energy and cell reproduction by facilitating thermodynamically advantageous reduction/oxidation (redox) reactions involving the transfer of electrons from electron donors to electron acceptors. This results in oxidation of the electron donor and reduction of the electron acceptor. Electron donors can include natural organic carbon and anthropogenic carbon compounds. Electron acceptors are elements or compounds that occur in relatively oxidized states and can accept electrons generated during substrate oxidation. Without the complete transfer of electrons to an electron acceptor, a substrate

cannot be fully oxidized. Electron acceptors commonly occurring in groundwater include oxygen, nitrate, Fe(III), sulfate, and carbon dioxide.

The driving force of biodegradation is electron transfer, which is quantified by the Gibbs free energy of the reaction (ΔG°_r) (Stumm and Morgan, 1981; Bouwer, 1994; Godsey, 1994). The value of ΔG°_r represents the quantity of free energy consumed ($\Delta G^\circ_r > 0$) or yielded ($\Delta G^\circ_r < 0$) to the system during the reaction. Although thermodynamics determines which reactions are energetically favorable, the rate at which the reactions actually occur does not depend on free energy change, but rather on the reaction mechanism (Chappelle, 1993). For example, if benzene and oxygenated water are mixed in the laboratory, benzene and oxygen do not immediately react to form carbon dioxide and water, even though this reaction is thermodynamically favorable. At the low ambient temperatures characteristic of the laboratory environment, collisions of oxygen and benzene molecules occur too infrequently and with insufficient force for the reaction to proceed. The *activation energy* represents the net expenditure of energy required to bring the molecules into close proximity, with sufficient force to initiate the required reaction. At a higher temperature (say, the combustion temperature of benzene), the necessary activation energy is available, and the molecules collide frequently, and with sufficient force to sustain the reaction. However, at the temperatures favored by living cells, benzene oxidation simply does not occur quickly enough by itself to be of use in energy production.

Living organisms solve this problem through the use of enzymes. Enzymes are proteins that catalyze chemical reactions in living cells, and work by combining chemically with a substrate or a combination of substrates, and bringing them into a configuration that enables a particular reaction to occur. The enzymatic combination thus provides the necessary activation energy, thereby facilitating the chemical reaction and generating the reaction products. This general behavior, common to many enzymatic reactions, is summarized by:

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$$enzyme \ + \ substrate \ \Rightarrow \ enzyme-substrate \ complex \ \Rightarrow \ enzyme \ + \ products$$

Although thermodynamically favorable, most of the reactions involved in biodegradation of fuel hydrocarbons or oxygenates cannot proceed abiotically because of the lack of activation energy. Microorganisms generate enzymes that are capable of providing the necessary activation energy; however, they will facilitate only those redox reactions that have a net yield of energy (i.e., $\Delta G^{\circ}_{r} < 0$). Even though considerable energy may be available to microorganisms facilitating particular reactions, the high activation energies associated with cleavage of some types of molecular bonds may render certain compounds, or classes of compounds, relatively recalcitrant. Microorganisms preferentially utilize electron acceptors while metabolizing hydrocarbons (Bouwer, 1992). DO is utilized first as the prime electron acceptor. After the DO is consumed, anaerobic microorganisms typically use native electron acceptors in the following order of preference: nitrate, manganese, ferric iron hydroxide, sulfate, and finally carbon dioxide. In addition, some compounds including chlorinated solvents and possibly MTBE may also be used as electron acceptors.

In addition to being controlled by the energy yield of the reaction, the expected sequence of redox processes also is a function of the oxidizing potential of the groundwater. This potential is a measure of the relative tendency of a solution or chemical reaction to accept or transfer electrons. As each subsequent electron acceptor is utilized, the groundwater becomes more reducing, and the oxidation/reduction potential (ORP) of the water decreases (Figure 2.3). The main force driving this change in redox potential is microbially mediated redox reactions. ORP can be used as an indicator of which redox reactions may be operating at a site. Environmental

ORP (mV)

| -1000 | -500 | 0 | +500 | +1000 |

O_2 Reduction

Denitrification

Manganese Reduction

Fe^{2+} ← Fe^{3+}

Sulfate Reduction

Methanogenesis

Higher

↑

Relative
Energy
Yield for
Redox
Reaction

↓

Lower
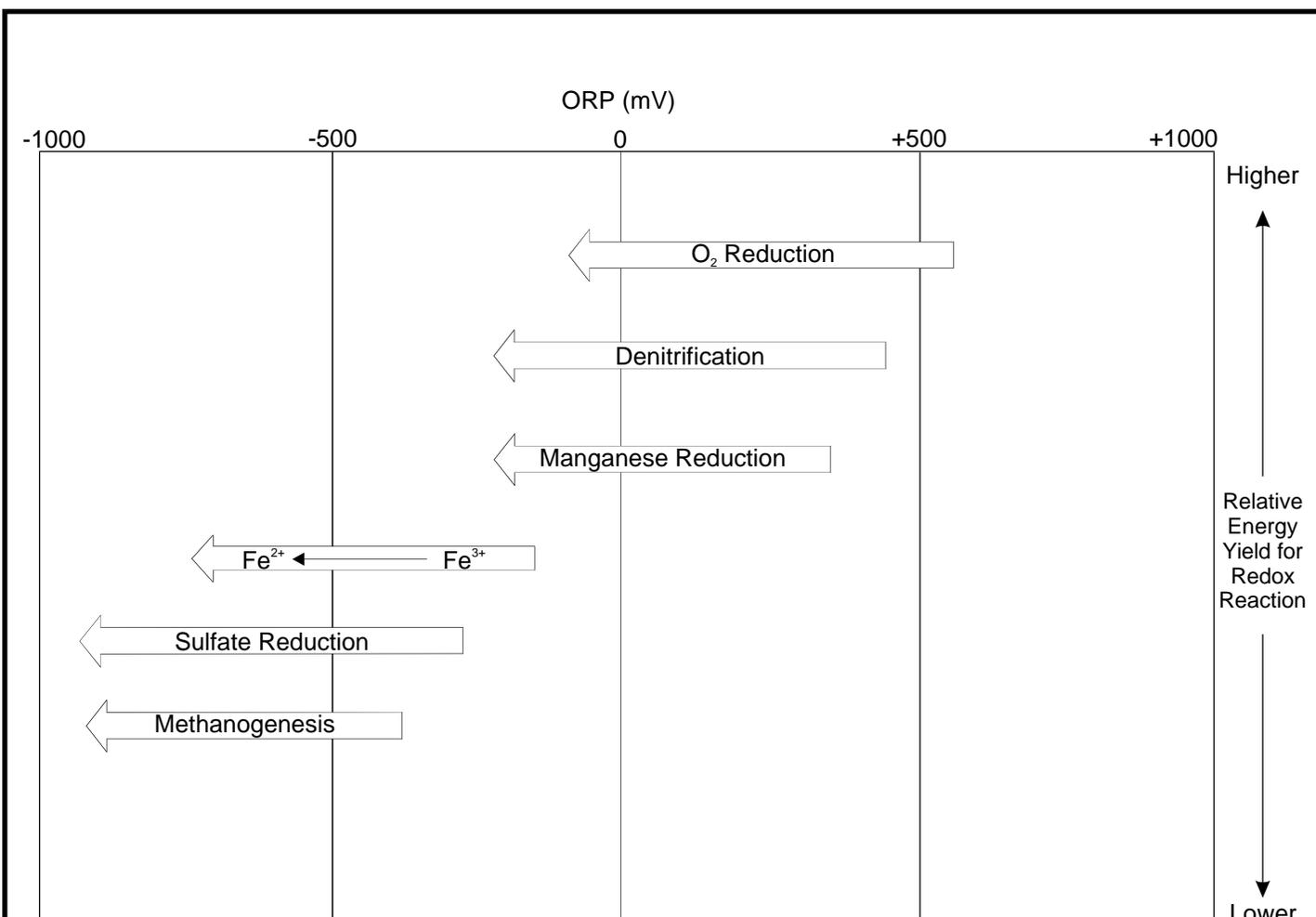
Notes

ORP = Oxidation Reduction Potential

1. These reactions would be expected to occur in sequence if the system is moving toward equilibrium.

2. These redox processes occur in order of their energy-yielding potential (provided microorganisms are available to mediate a specific reaction). Reduction of a highly oxidized species decreases the ORP of the system.

3. The ORP of the system determines which electron acceptors are available for organic carbon oxidation.

4. Redox sequence is paralleled by an ecological succession of biological mediators.

Adapted from Stumm and Morgan, 1981.

FIGURE 2.3

SEQUENCE OF MICROBIALLY MEDIATED REDOX PROCESSES

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conditions and microbial competition ultimately determine which processes will dominate.

Depending on the types and concentrations of electron acceptors present (e.g., nitrate, sulfate, carbon dioxide), pH conditions, and ORP, anaerobic biodegradation can occur under denitrifying, Fe(III) reducing, sulfate reducing, or methanogenic conditions. Other, less common anaerobic degradation mechanisms such as manganese reduction may predominate if the physical and chemical conditions in the subsurface favor use of these electron acceptors.

2.7.2 Chemical Degradation as a First-Order Process

To properly account for biodegradation at the microscopic level, one must accurately describe such parameters as nutrient availability, cellular diffusion, cellular growth dynamics, the microscopic dimensions of individual pores, interpore substrate concentrations, and factors controlling potential changes in soil porosity and permeability. These parameters must then be incorporated into a nonlinear mathematical representation of process dynamics (Baveye and Valocchi, 1989). Fortunately, this level of effort is not necessary at many sites. Two of the principal models proposed by researchers to describe degradation processes at the cell level (the biofilm and Monod kinetic models) can be simplified to a first-order kinetic approximation under certain limiting conditions (Bouwer and McCarty, 1984; MacQuarrie *et al.*, 1990). In addition, several authors have noted that first-order, or pseudo first-order kinetics approximate the rate of hydrocarbon degradation observed at individual study sites (Berry-Spark *et al.*, 1988; Chiang *et al.*, 1989; Dragun, 1988; Gillham and O'Hannesin, 1994; Kemblowski *et al.*, 1987).

The use of first-order kinetics assumes that the rate of change in chemical concentration with time (*t*) is dependent only on the concentration of the chemical in soil or groundwater (*C*). Ranges of first-order rate constants have been estimated and tabulated for a number of organic chemicals (see, for example, Howard *et al*., 1991). Site-specific, historic chemical concentration information also can be used to estimate site-specific first-order rate constants, as long as the apparent degradation rate can be normalized to account for the

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effects of dilution, dispersion, and sorption. One method for determining first-order rate constants for BTEX compounds was proposed by Buscheck and Alcantar (1995). The Buscheck and Alcantar (1995) method derives a relationship that allows calculation of first-order biodegradation rate constants for steady-state plumes. This method involves coupling the regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) with an analytical advection-dispersion equation for one-dimensional, steady-state contaminant transport (Bear 1979). Additional parameters that must be estimated to calculate the first-order rate constant include the retarded longitudinal velocity of the contaminant. Application of the method is discussed in detail in other documents (e.g., AFCEE Technical Protocol, 1995).

Decay rates computed using the Buscheck and Alcantar method account for chemical (abiotic) decay and biological (aerobic and anaerobic) decay. For an expanding plume, this first-order approximation can be viewed as an upper bound on the biodegradation rate. Use of this method results in overestimation of the rate of biodegradation because a typical expanding plume exhibits decreasing source area concentrations, increasing downgradient concentrations, or both, as a consequence of source area dispersion and downgradient advection. Over time, these changes result in a decreasing slope on a log-linear plot, and consequently a decreasing biodegradation rate. In addition, the magnitude of the decay rate calculated using the Buscheck and Alcantar method is sensitive to the estimated migration velocity of the contaminant along the selected flowpath; therefore, inaccuracies in the estimated velocity will cause estimates of first-order rate constants to be less accurate. Overestimation of the groundwater velocity will result in overestimation of the decay rate, and vice versa.

2.7.3 Potential for Biodegradation of MTBE

Ethers, including MTBE, comprise a class of compounds that are characteristically unreactive over a wide range of conditions (Church *et al*., 1997), and are generally difficult to degrade biologically (Jensen and Arvin, 1990). MTBE can react with hydroxyl

radicals in the aqueous phase (Barreto *et al*., 1995), yielding TBF as a degradation product (Figure 2.4). However, the primary MTBE degradation pathway that leads to formation of TBF is reported (Church *et al*., 1997) to be atmospheric photo-oxidation; and because it is readily hydrolyzed to TBA, TBF does not accumulate in the environment. The known pathways for MTBE degradation in surface water, soil, and groundwater are microbially-mediated hydrolysis, oxidation under aerobic conditions, and reduction under anaerobic conditions (Church *et al*., 1997). The principal product of both hydrolysis and reduction is TBA, which can also be biologically degraded, although at very low rates (Hickman and Novak, 1989; Yeh, 1992; Church *et al*., 1997). TBA is degraded by demethylation to 2-propanol, which is oxidized to acetone or methyl acetate (Figure 2.4).

Although TBA is an indicator of MTBE degradation, the mere presence of TBA is not conclusive evidence of degradation in field situations. This is because TBA also can be used as a fuel additive (Buxton *et al*., 1997). To complicate matters, current methods of analysis for TBA are generally not capable of achieving the low detection limits required to measure TBA concentrations in environmental samples (Church *et al*., 1997; Happel *et al*., 1998).

In general, most investigators have concluded that MTBE is difficult to biodegrade, and some researchers have classified MTBE as recalcitrant, which means that no degradation was observed under the conditions, and within the time frames used for their examination (Squillace *et al*., 1997). The difficulty with which MTBE degrades may result from the resistance to microbial action of the tertiary or quarternary carbon

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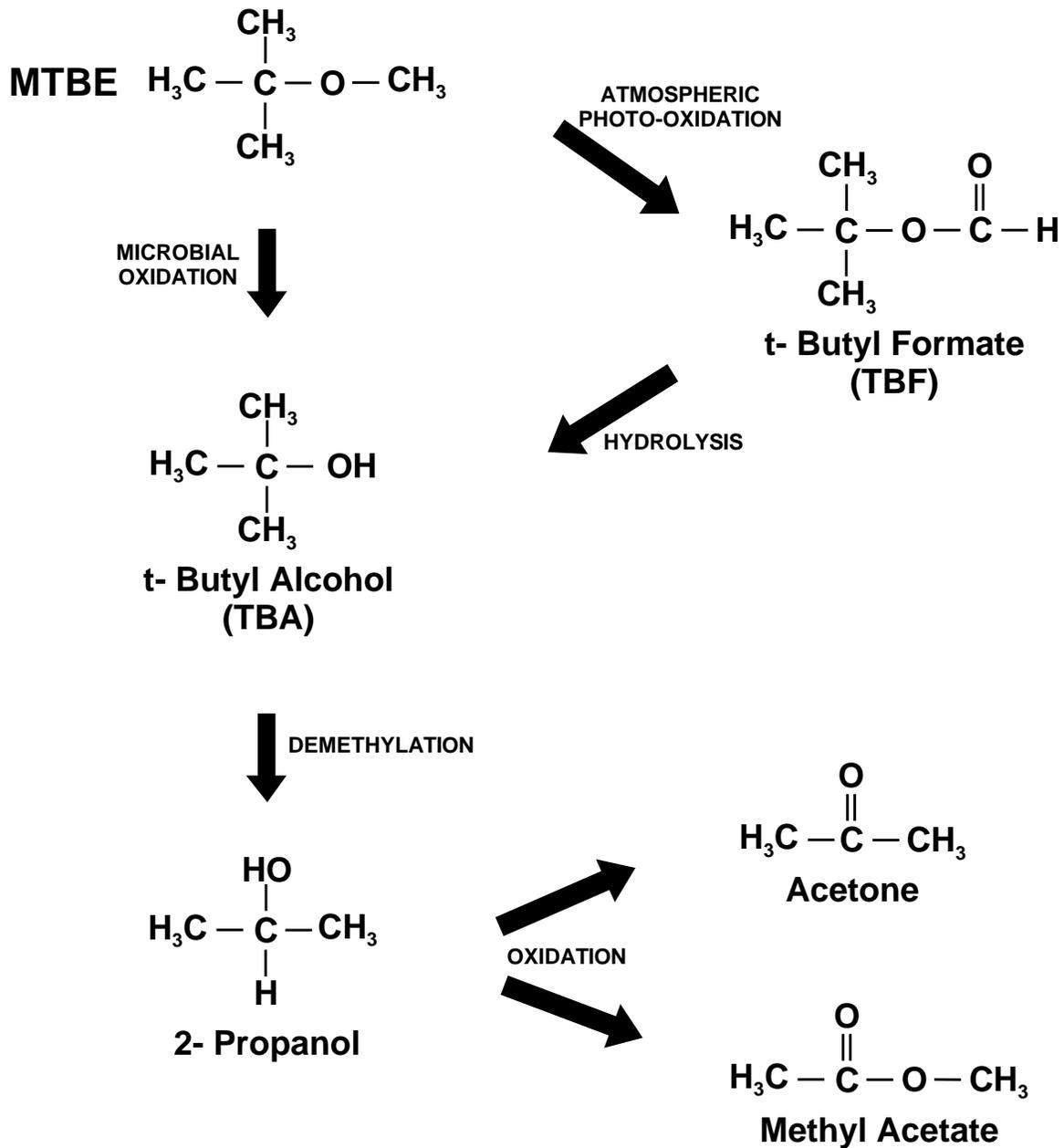
FIGURE 2.4

SEQUENCE OF MTBE
DEGRADATION REACTIONS

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atoms (Suflita and Mormile, 1993) or the stable and unreactive ether bond (Mormile *et al.*, 1994; Yeh and Novak, 1994).

Ideally, in order to evaluate the degradation of MTBE, time-series data for numerous microcosms and field sites, representing a range of chemical and environmental conditions and collected over long periods of time, should be compiled and examined. In reality, a relatively small number of investigators have examined MTBE degradation using microcosm studies; and because the BTEX compounds are typically the constituents of concern associated with gasoline spills, most field-scale investigations have concentrated on the fate of BTEX compounds, and neglected MTBE (Happel *et al.*, 1998). However, despite its apparent recalcitrance, and the relative scarcity of MTBE research, MTBE degradation has occasionally been reported. The results of microcosm and field-scale assessment of MTBE degradation are summarized in Tables 2.3 and 2.4, and discussed in the following sections.

2.7.4 Microcosm Investigations of MTBE Degradation

Jensen and Arvin (1990) conducted batch tests under aerobic conditions, using sandy aquifer material, topsoil, and activated sludge as the inoculum (Table 2.3). The slurry of aquifer material was observed for 60 days, while the slurries of topsoil and activated sludge were observed for 40 days. No biodegradation of MTBE was observed under these conditions. By contrast, BTEX constituents and naphthalene were completely degraded within 13 days in the aquifer microcosm, and within nine days in the topsoil and activated sludge microcosms. The possible interference of MTBE in degradation of the aromatic hydrocarbons also was evaluated. At an MTBE concentration of 200 mg/L, the length of time required to completely degrade ortho- and meta-xylene was increased by one day.

Suflita and Mormile (1993) evaluated the biodegradability of MTBE and other ether compounds in a microcosm study, using aquifer material from a methanogenic section

TABLE 2.3
SUMMARY OF MTBE MICROCOSM STUDIES
MTBE TECHNICAL SUMMARY REPORT

Source	Aerobic Degradation Detected?	Anaerobic Degradation Detected ?	Anaerobic Process	Was TBA Analyzed for?	Was TBA detected?	Incubation Period (Days)
Jensen and Arvin (1990)	No	NA[a/]	NA	No	NA	60
	No	NA	NA	No	NA	40
Sullita and Mormile (1993)	NA	No	methanogenesis	No[b/]	NA	182
Mormile *et al*. (1994)	NA	Yes[c/]	methanogenesis	Yes	Yes	152
	NA	No	sulfate reduction	Yes	No	244
	NA	No	denitrification	Yes	No	85
Yeh and Novak (1994)	NA	Yes[d/]	methanogenesis	Yes	Yes	250
	NA	No	sulfate reduction	Yes	No	250
	NA	No	denitrification	Yes	No	250
Yeh and Novak (1995)	No	NA	NA	Yes	No	90
	No	NA	NA	Yes	No	100
Salanitro *et al.* (1994)	Yes	NA	NA	Yes[e/]	Yes	1
Horan and Brown (1995)	Yes	NA	NA	No[f/]	NA	0 to 4
Cowan and Park (1996)	Yes	NA	NA	Yes	Yes	4
Mo *et al*. (1997)	Yes	NA	NA	No[f/]	NA	7 to 14
Steffan *et al*. (1997)	Yes	NA	NA	Yes[e/]	Yes	1
Eweis *et al*.(1998)	Yes	NA	NA	No	NA	4 to 13

[a/] NA = Not analyzed.

[b/] Pressure increased resulting from biogas formation (methane and carbon dioxide) were monitored with a pressure transducer. Methane and MTBE concentrations were measured at the end of the incubation period.

[c/] Methanogenic degradation only observed in sewage impacted creek sediments. No degradation was observed in soil from a gasoline impacted aquifer or sediments from a fuel impacted river.

[d/] Degradation was only observed in oligotrophic soils low in organic material. MTBE was recalcitrant under methanogenic conditions in organic rich soils.

[e/] MTBE degradation was also confirmed with the measurement of carbon dioxide.

[f/] MTBE degradation was confirmed with the measurement of carbon dioxide.

Site	Field Results								Associated Laboratory Results				
	MTBE Degradation				Presence of Degradation Products		Aquifer Conditions						
	Age of Spill (years)	Was MTBE Biodegradation Measured?/ Observed?	First-Order Degradation Rate Constant (day⁻¹)	Estimated Percent Removal by Natural Attenuation	Was TBA Analyzed?/Detected?	Method Used	Was the Aquifer Aerobic or Anaerobic?	Dominant Processes	Associated Microcosms Studies	First Order Decay Rate (day⁻¹)	Removal Efficiency	Was TBA Analyzed For?/Detected?	Environmental Conditions
UST Site, Sampson County, North Carolina [a]	~11	Yes/Yes	0.001 (near source) 0.0008 (down-gradient) 0 (distal edge of plume)	N/A [b]	No	N/A	Aerobic -- Anaerobic in plume core	Denitrification	Yes	N/A	29% to 52%	Yes/Yes	Aerobic
MTBE Degradation Experiment, CFB Borden [c]	7.4 to 8.2	Yes/Yes	0.0012	97	Yes/No	Church *et al.*, 1997	Aerobic	Not confirmed	Yes	Degradation observed but rate not	N/A	Yes/No	Aerobic
USGS UST Field Site, Laurel Bay Exchange, Beaufort, South Carolina [d]	7 to 8	No/No	N/A	N/A	Yes/Yes	Church *et al.*, 1997	Anaerobic	Iron Reduction	Yes	N/A	3%	No	Iron Reducing
South Platte River Two-Plume Site, Denver Colorado [e]	~10	Qualitatively/No Degradation was Observed	N/A	N/A	No	N/A	Aerobic	Sulfate Reduction Denitrification Iron Reduction Methanogenesis	No	N/A	N/A	N/A	N/A
Leaking Underground Storage Tank Site, East Patchogue, New York [f]	7 to 15	No/No	N/A	N/A	No	N/A	Where Oxygen is Present (>1.0 mg/L) in the Groundwater, MTBE is Absent (<20 µg/L) (USEPA, 1998)	No Methane	No	N/A	N/A	N/A	N/A
US Coast Guard Support Center, Fuel Farm Site [g]	N/A	Yes/Yes	0.008 (USEPA, 1998c) 0.004 (Wilson *et al.*, 1999)	N/A	Yes/Yes	GC/MS [h]	Anaerobic	Methanogenesis	Yes	0.007 to 0.009	N/A	N/A	Methanogenic
US Coast Guard Support Center, Fire Station Site [i]	< 10	Yes	0.0012 (field) 0.0003 (BioSCREEN) [j] 0.0008 (BioSCREEN) [j]	N/A	N/A	N/A	Anaerobic	Sulfate Reduction Iron Reduction	No	N/A	N/A	N/A	N/A
Service Station UST Site, Michigan [k]	N/A	No/Concentrations of MTBE were Observed to Decrease to Below Detectable Levels	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

[a] Daniel, 1995; Borden, 1997; API, 1997.

[b] N/A = not available.

[c] Hubbard *et al.*, 1994; Barker *et al.*, 1998; Schirmer and Barker, 1998.

[d] Landmeyer *et al.*, 1996; Buxton et al., 1997; Landmeyer *et al.*, 1998.

[e] McMahon and Bruce, 1997.

[f] Weaver *et al.*, 1996; USEPA 1998c.

[g] USEPA 1998c; Hurt *et al.*, 1999; Wilson *et al.*, 1999.

[h] GC/MS = Gas chromatagraph/mass spectrometer.

[i] USEPA 1998c, Wilson *et al.*, 1999.

[j] Rate constant estimated using calibrated transport model.

[k] Pavne *et al.*, 1997.

of an anaerobic aquifer contaminated by landfill leachate (Table 2.3). After a 182-day incubation period, no degradation of MTBE was observed.

In a microcosm composed of soil dredged from the Ohio River, Mormile *et al.* (1994) observed MTBE degradation to TBA after 152 days under methanogenic conditions (Table 2.3). The pH for the microcosm slurry was reported to be 7.0 to 7.2. MTBE degradation was not observed in soils from a leachate-contaminated aquifer, a gasoline-contaminated aquifer, or sediment from a creek in Cincinnati, Ohio.

Yeh and Novak (1994) evaluated MTBE biodegradation under anaerobic conditions in microcosms constructed of soils from three sites (Table 2.3). The soils contained a widely-varying range of naturally-occurring organic matter; microcosm studies were conducted under denitrifying, sulfate-reducing, and methanogenic conditions. MTBE was observed to degrade only in soils depleted in natural organic material; degradation preferentially occurred at a pH between 5.0 and 6.0. Degradation occurred under methanogenic conditions only with the addition of nutrients. MTBE was not degraded in any of the unamended microcosms over a 250-day incubation period. In a subsequent evaluation, conducted under aerobic conditions, Yeh and Novak (1995) found that MTBE was not degraded after more than 100 days of incubation. The results of the Yeh and Novak (1994 and 1995) microcosm investigations suggest that MTBE degradation may occur only when other sources of degradable organic matter are limited.

MTBE degradation was observed by Salanitro *et al.* (1994) in a mixed bacterial culture developed from a chemical plant biotreater sludge (Table 2.3). Experiments were conducted under aerobic conditions by supplying pure oxygen to the culture. Generation of TBA as an intermediate product of degradation was observed.

Horan and Brown (1995) found that MTBE could be degraded under aerobic conditions using continuous culture enrichments (Table 2.3). When concentrations of MTBE in the microcosm were increased to approximately 740 mg/L, the degradation of

the fuel constituent hexadecane was inhibited. These results are consistent with the findings of Jensen and Arvin (1990), who also identified inhibition of biodegradation at elevated MTBE concentrations (above).

Aerobic degradation of MTBE also was observed by Cowan and Park (1996) in undefined mixed cultures enriched from an activated sludge and petroleum refinery wastewater (Table 2.3). Formation of TBA, consistent with Salinitro *et al.* (1994), was observed and evaluated; biodegradation kinetics confirmed that TBA degradation occurred at a rate slower than MTBE degradation.

Pure bacterial cultures isolated from activated sludge and the fruit of the Gingko tree by Mo *et al.* (1997) were capable of MTBE degradation (Table 2.3). Experiments were conducted under aerobic conditions with MTBE as the sole source of carbon.

Steffan *et al.* (1997) were able to degrade MTBE under aerobic conditions using a bacterial culture acclimated to propane (Table 2.3). However, the bacteria were not capable of utilizing MTBE as the sole substrate. Degradation was confirmed by the production of stoichiometric amounts of TBA. Consistent with the results of Cowan and Park (1996), TBA degradation was observed to be slower than MTBE degradation.

Eweis *et al.* (1998) evaluated MTBE degradation in a microcosm constructed using a mixed microbial culture, developed from a compost-based biofilter (Table 2.3). MTBE degradation was observed to occur, and was not slowed by the presence of other organic contaminants.

2.7.5 Field-Scale Investigations of MTBE Degradation

As a consequence of the relatively recent introduction of MTBE as a constituent of petroleum fuels, fewer field-scale investigations than microcosm studies have been completed to evaluate the degradation of MTBE in the natural environment. The available information regarding field-scale investigations of MTBE biodegradation is summarized in Table 2.4. Most field investigations that have been reported involve gasoline storage

facilities (USTs), having a long history of use, with possible product loss occurring prior to the introduction of MTBE as a fuel oxygenate. Therefore, BTEX contamination may in many instances precede MTBE contamination (Happel *et al.*, 1998).

2.7.5.1 UST Site, Sampson County, North Carolina

Gasoline and No. 2 fuel oil from USTs contaminated a shallow coastal-plain aquifer in rural North Carolina (Daniel, 1995; Borden, 1997; Borden *et al.*, 1997; API, 1997). The unconsolidated deposits in the subsurface consist of silty to clayey sand, and the water table is at a depth of about five to six feet below ground surface (bgs). A mixed BTEX (primarily benzene and ortho-xylene) plume extends more than 550 feet downgradient from the source area. The highest concentrations of MTBE (about 10 mg/L) and benzene (about 17 mg/L) were detected in groundwater samples from wells near the former UST location. Concentrations decreased along the flowpath to about 0.3 mg/L (MTBE) and 0.2 mg/L (benzene) at the most distal sampling location.

The hydraulic conductivity of the aquifer ranges from 1 to 4 feet per day (ft/day), and averages about 2.6 ft/day. The estimated effective porosity is 0.10, and the calculated groundwater flow velocity ranges from 13 to 54 feet per year (ft/yr), with an average velocity of 39 ft/yr. A transport velocity was estimated for MTBE, using a three-dimensional solution to the advection-dispersion solute transport equation. The estimated MTBE transport velocity (57 ft/yr) was similar to the maximum estimated groundwater flow velocity, suggesting that MTBE was preferentially migrating along more-permeable flowpaths.

The background concentrations of dissolved oxygen (7 to 8 mg/L) indicated that, in the absence of hydrocarbon contamination, conditions in the aquifer were relatively aerobic. Dissolved oxygen concentrations decreased to below 0.5 mg/L along the plume axis. Background concentrations of dissolved nitrate ranged from 7 to 17 mg/L; and dissolved sulfate ranged from "not detected" to 8 mg/L. There was no apparent spatial association between sulfate concentrations and the distribution of fuel constituents. The

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concentrations of dissolved iron were low to "not detected" at most locations; however, higher concentrations of dissolved iron (1 - 2 mg/L) were detected in groundwater samples from the more highly contaminated parts of the site. The ORP ranged from about +200 millivolts (mV) to +450 mV, indicative of oxidizing conditions, and the pH of the shallow groundwater was 4.3.

The degradation rate for MTBE was estimated by comparing the mass flux of MTBE through the aquifer at a location near the source area with the mass flux of MTBE at three downgradient locations, distal from the source. The estimated first-order degradation rate constant was greatest near the source area (0.001 - 0.0018 day^{-1}), becoming insignificant beyond a distance of about 300 feet downgradient. This suggested that most MTBE degradation was occurring near the source area. The principal degradation mechanisms were thought to be aerobic respiration and denitrification.

These results were subsequently confirmed by a microcosm study (Daniel, 1995). Soil was collected from beneath the water table at three locations – 35 feet, 100 feet, and 200 feet downgradient from the source. Soil from each location was used to construct four different microcosms: sterilized control, aerobic, anoxic, and anaerobic. Every microcosm was split; the microcosms were then spiked with a solution containing BTEX compounds and MTBE, and the split microcosms were spiked with a solution of MTBE only. The effects of ammonia amendment also were examined, using the microcosms constructed from soil samples nearest the source (35 feet) and furthest from the source (200 feet).

MTBE was degraded aerobically in the microcosms constructed using soil collected nearest the source. Degradation apparently began after a 20-day lag period, and MTBE concentrations decreased from an initial concentration of 2.1 mg/L to between 1.0 and 1.5 mg/L after a period of 93 days, with no significant degradation subsequently occurring. TBA was detected as a product of MTBE degradation. The highest concentration of

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TBA detected in any microcosm was 0.35 mg/L, which was detected concurrently with a reduction of 0.45 mg/L in the concentration of MTBE in the same microcosm.

No MTBE degradation was observed under anaerobic conditions. The addition of BTEX or ammonia to aerobic microcosms did not appear to enhance or inhibit MTBE biodegradation, as compared with microcosms containing MTBE alone.

The lag period noted in aerobic microcosms constructed during this investigation appears to be a common feature of MTBE degradation. The lag period or acclimation phase has been defined as a change in a microbial community effected by exposure to a chemical resulting in faster biotransformation of that substance (Hickman and Novak, 1989). Possible mechanisms for acclimation include the following:

- enzyme induction,

- mutation or genetic transfer

- growth of the active population(s),

- preferential use of other organic substrates before the compound of interest,

- inactivation or degradation of toxins or inhibitors, and

- limitation of growth rates by nutrient supply or protozoan grazing.

Conversely, Borden *et al*. (1997) provide several possible explanations for cessation of MTBE biodegradation in microcosms, including:

- buildup of inhibitory degradation products;

- presence of a minimum degradable concentration; or

- depletion of required nutrients or co-substrates.

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2.7.5.2 MTBE Degradation Experiment, CFB Borden

A long-term experiment was conducted under controlled conditions at Canadian Forces Base (CFB) Borden, Ontario, Canada (Hubbard *et al*., 1994; Barker *et al*., 1998; Schirmer and Barker, 1998). A known volume (about 2,800 L) of native groundwater containing a mixture of 90 percent gasoline and 10 percent MTBE (initial concentration of 269 mg/L) and a tracer (chloride) was introduced to an aquifer in the shallow subsurface to assess the fate and transport of MTBE and determine whether MTBE affects the migration of BTEX compounds.

The earth materials in the subsurface at CFB Borden are glaciofluvial deposits consisting of horizontal, discontinuous strata of medium- to fine-grained sand, with irregular lenses of coarse sand and silty clay. The hydraulic conductivity of the aquifer averages about 6 meters per day (m/d; equivalent to 20 ft/day), and ranges across two orders of magnitude, depending on location. The estimated effective porosity is 0.33, and the calculated groundwater flow velocity ranges from 0.005 m/d to 0.1 m/d (0.02 to 0.03 ft/day). The water table in the unconfined aquifer system is at a depth of 0.5 to 1.5 meters (1.5 to 5 feet) below land surface, and fluctuates seasonally. Vertical gradients in the shallow aquifer are negligible.

The shallow groundwater system is aerobic (dissolved oxygen concentrations ranging up to 8.5 mg/L), has a neutral pH, and contains low levels of nitrate (less than 0.7 mg/L) and dissolved organic carbon (0.7 mg/L to 15.8 mg/L). Sulfate concentrations range from 10 to 30 mg/L.

After a period of 476 days had elapsed, a number of groundwater samples were collected from numerous sampling points, and were analyzed. Virtually no mass loss of MTBE had occurred, and it was concluded (Hubbard *et al*., 1994) that MTBE degradation was not a significant removal mechanism.

After a subsequent period of about eight years had elapsed, another round of detailed groundwater monitoring was completed (Barker *et al.*, 1998). Groundwater samples were analyzed for MTBE and its potential degradation products TBA and TBF. Samples were analyzed at the Oregon Graduate Institute using the direct aqueous injection-gas chromatograph/mass spectrometer (DAI GC/MS) technique described by Church *et al.* (1997; [Appendix D]). The detection limits for this analysis were 0.1 g/L for MTBE, 0.1 g/L for TBA, and 10 g/L for TBF. Neither TBA nor TBF was detected in any groundwater sample. Barker *et al.* (1998) discuss several possibilities for the apparent absence of MTBE biodegradation products:

- MTBE was not biodegraded;

- TBA and TBF may be biodegraded rapidly; or

- As a consequence of the slow biodegradation rate of MTBE, TBA and TBF may be present but at concentrations less than the method detection limit.

The mass of MTBE remaining in the aquifer was estimated from the monitoring results, and it was concluded that less than three percent of the initial mass of MTBE remained. The investigators attributed the mass loss of MTBE to biodegradation, and estimated a first-order rate constant of 0.0012 day^{-1}. This degradation rate was supported using a numerical modeling evaluation of MTBE transport in groundwater.

A laboratory microcosm experiment was then conducted using aquifer material from CFB Borden and native groundwater (Barker *et al.*, 1998). Twenty-five microcosms were established and maintained under aerobic conditions. Sixteen of the batches were active microcosms (eight tests, with duplicates), and nine were sterile controls. MTBE concentrations decreased significantly in two, and perhaps three active microcosms, but did not change in the sterile microcosms, suggesting mass loss of MTBE due to biodegradation. No MTBE degradation products (TBA or TBF) were detected during the

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microcosm studies. The methods of chemical analyses and method detection limits were not explicitly stated by the authors.

2.7.5.3 U.S. Geological Survey UST Field Site, Laurel Bay Exchange, Beaufort, South Carolina

Gasoline contamination of a shallow aquifer occurred as a result of product loss from a UST at the Laurel Bay Exchange, Port Royal Island, Marine Corps Air Station, in Beaufort, South Carolina (Landmeyer *et al.*, 1996; ibid., 1998; Buxton *et al.,* 1997). An estimated volume of 5,700 L of gasoline is thought to have leaked from the tank shortly before the leak was detected in 1991. The UST and surrounding soil were removed in October 1994. The site is being investigated by the USGS to evaluate the natural attenuation of MTBE as compared with BTEX.

The unconsolidated deposits which form the shallow aquifer consist of 45 feet of silty, well-sorted sand. This sand is underlain by a regionally extensive clay aquitard. The depth to water in the unconfined aquifer averages about 13 feet. As a consequence of aerobic conditions in the subsurface, and the shallow depth to water, many of the sand grains have a ferric hydroxide coating. The frequency of occurrence of iron hyroxide coatings on sand grains was found (by visual inspection) to decrease in areas having elevated concentrations of fuel constituents in groundwater.

The hydraulic conductivity of the aquifer was estimated to be 11 ft/day. The groundwater velocity was estimated to be approximately 70 ft/yr near the former tank location, and increased in the downgradient direction to approximately 500 ft/yr. Groundwater flow velocities and direction were evaluated from 1993 to 1997 and were found to be consistent through this time.

Groundwater monitoring was conducted periodically between 1993 and 1997. Groundwater samples were collected from 15 monitoring wells and five multi-port samplers. These samples were analyzed for total petroleum hydrocarbon (TPH) compounds, BTEX constituents, MTBE, and potential MTBE degradation products

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(TBA and TBF). TBA and TBF were analyzed using the DAI GC/MS technique (Church *et al.*, 1997), with detection limits of 0.1 g/L and 5 g/L, respectively. Potential electron acceptors and microbially-generated degradation byproducts also were analyzed. The analytes included dissolved hydrogen, ferrous iron, [Fe(II)], sulfide, sulfate (SO_4^{-2}), methane (CH_4), dissolved inorganic carbon, and dissolved oxygen (Buxton *et al.*, 1997).

BTEX compounds were detected in groundwater samples from eight wells, at concentrations ranging from 0.006 mg/L (ethylbenzene) to 22.5 mg/L (toluene). MTBE was detected in groundwater samples from seven wells, at concentrations ranging from 0.22 mg/L to 251 mg/L. TBA also was detected in groundwater samples from several wells, at concentrations ranging up to 5 mg/L. TBA was only detected in groundwater samples from wells that also contained MTBE; however, TBA could not be directly related to MTBE degradation because TBA also may have been a fuel oxygenate at this site.

Dissolved oxygen concentrations ranged from about 5.9 mg/L, in areas peripheral to the plume, to below detection limits along the plume axis. Groundwater samples from wells along the plume axis also contained sulfide, and higher concentrations of dissolved iron [Fe(II)] than were detected at other locations.

A series of microcosm studies was conducted, using earth materials and microbial consortia collected *in-situ* from the site (Landemeyer *et al.*, 1998). Approximately three percent of radio-labeled MTBE (MTBE generated using radioactive carbon) was completely mineralized to radio-labeled carbon dioxide after a seven-month incubation period under iron-reducing conditions.

2.7.5.4 South Platte River Two-Plume Site, Denver, Colorado

In the early to mid-1980s, petroleum fuel from two sources leaked into an alluvial aquifer bordering the South Platte River, near central Denver, Colorado (McMahon and Bruce, 1997). Fuel originating at one source consisted of non-oxygenated gasoline and

diesel fuel, and fuel from the other source consisted of gasoline with MTBE. The aquifer is composed of unconsolidated sands and gravels. The water table is about 12 feet below land surface, and the shallow groundwater system is in hydraulic communication with the South Platte River, which provides a continuing source of dissolved nitrate, sulfate, and organic carbon to the aquifer.

The configuration of the water table is such that the hydrocarbon plumes emanating from the two sources are separated near the source areas, but merge a few hundred feet downgradient. The spatial distribution, and seasonal variation in concentrations of electron acceptors (nitrate, sulfate, oxygen) and biodegradation products (ferrous iron, methane, hydrogen) indicated that BTEX compounds were readily degraded, primarily under sulfate-reducing conditions. However, conditions in the plumes displayed spatial and seasonal variation, so that at particular locations and times, hydrocarbon degradation also occurred under denitrifying, iron-reducing, and methanogenic conditions. No evidence of MTBE degradation was observed.

2.5.7.5 Leaking Underground Storage Tank Site, East Patchogue, New York

Several residential wells in East Patchogue, Long Island, New York, were contaminated by gasoline constituents, including MTBE, that originated at leaking USTs beneath an abandoned service station (Weaver *et al*., 1996; USEPA, 1998c). Principal investigators (Weaver *et al*., 1996) used analytical data for BTEX constituents and MTBE to estimate the mass of fuel constituents in groundwater, the volume of gasoline released, and local groundwater flow velocities.

Groundwater in southern Long Island occurs in glacial outwash deposits, consisting of clean sands and gravels. The organic carbon content of the unconsolidated materials was determined to be about 0.13 percent, and the effective porosity was estimated to be 0.30. The hydraulic conductivity of the upper glacial aquifer at the site is on the order of 40 to 80 ft/day, and groundwater flow velocities were estimated to be as great as 1 ft/day.

Data from a three-dimensional monitoring network, which included 22 monitoring wells and 26 multi-level samplers, were used to estimate the mass and configuration of the BTEX and MTBE plumes. Samples were collected on three separate occasions in 1994 and 1995, so that the temporal evolution of the plumes could be examined. BTEX constituents were consistently detected in groundwater samples collected near the original locations of the USTs, and each was detected in groundwater at one or more locations longitudinally along the BTEX plume, indicating that gasoline in the subsurface continued to function as a source of fuel constituents in groundwater. However, the estimated total mass of BTEX constituents in groundwater decreased with time, indicating even though BTEX was continuing to migrate into the aquifer from the source area in the former tank location, BTEX mass was being depleted more rapidly than it was added, primarily as a consequence of biodegradation.

By contrast, no clear temporal trend in total mass of MTBE in the plume was observed through the duration of monitoring. MTBE was not detected in groundwater samples collected from wells near the source of fuel constituents; nor was MTBE detected in groundwater samples collected from locations between the source area and a point about 2,000 feet downgradient of the source. This suggested that MTBE had completely leached from the gasoline in the source area by the time groundwater monitoring was initiated.

Groundwater samples were not analyzed for TBA or TBF. MTBE was not detected in groundwater samples having an oxygen content greater than about 1 mg/L suggesting (USEPA, 1998c) that MTBE persisted in a "shadow" zone, depleted in oxygen, downgradient of the source area. The investigators concluded that biodegradation of MTBE was not occurring; and biodegradation rates were not estimated.

The leading edge of the MTBE plume eventually migrated more than 6,000 feet downgradient from the gasoline source (the leaking USTs). The center of mass of the MTBE plume migrated approximately 1,500 feet further downgradient than center of

mass of the BTEX plume, illustrating the differences in fate and transport properties between MTBE and other fuel constituents.

2.7.5.6 U.S. Coast Guard Support Center, Elizabeth City, North Carolina

A jet-fuel spill (JP-4) at the US Coast Guard Support Center, Elizabeth City, North Carolina contaminated groundwater with BTEX compounds and MTBE (USEPA, 1998c). Fuel constituents have apparently migrated to groundwater over a period of "decades." The site is located in the floodplain of the Pasquotank River; the shallow aquifer consists of unconsolidated alluvial deposits with groundwater occurring at a depth of about 10 feet bgs. Hydraulic conductivity of the groundwater system ranges from 0.005 to 0.33 centimeters per second (cm/sec; equivalent to 14 to 940 ft/day).

Benzene concentrations ranged from 0.033 mg/L to 2.3 mg/L, and MTBE concentrations ranged from 0.001 mg/L to 3.9 mg/L. The highest concentration of dissolved oxygen was 1.3 mg/L, and oxygen concentrations were less than 0.1 mg/L in most samples, indicating that the groundwater system was largely anaerobic. Methane was detected in all groundwater samples at concentrations ranging up to 10.6 mg/L, indicating that methanogenesis was occurring.

A first-order rate constant for MTBE degradation (0.008 day^{-1}) was estimated by conducting a linear regression of MTBE concentrations in groundwater versus travel time for sampling points located along a flowpath extending from the source area to a downgradient location (the method of Buscheck and Alcantar). Laboratory microcosm studies were conducted to further evaluate MTBE degradation (Wilson *et al*., 1999). Microcosms were constructed using sediment collected from a location along the groundwater flowpath, downgradient of the source area. One treatment consisted of MTBE, together with BTEX and trimethylbenzenes (TMB), at concentrations representative of *in-situ* conditions in the aquifer. A second treatment contained MTBE alone. Sterile (autoclaved) control microcosms were also prepared. The first-order degradation rate estimated for MTBE in the MTBE/BTEX/TMB microcosms after 500

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days of incubation was 0.009 day^{-1}; and the first-order degradation rate estimated for MTBE in the MTBE microcosms was 0.007 day^{-1}. Loss of MTBE mass in the sterile controls was negligible (Wilson *et al*., 1999).

Results of the field investigation and microcosm studies were evaluated (Wilson *et al*., 1999) using an analytical model of contaminant fate and transport (BIOSCREEN). First-order rate constants similar to those derived from the microcosm studies were initially used in simulations; however, the results of simulations projected MTBE attenuation that was more extensive than actually observed in the field investigations. When the model was calibrated to field data, the calibrated first-order rate constant for MTBE degradation (0.004 day^{-1}) was about one-half the rate estimated using the results of the microcosm studies (Wilson *et al*., 1999).

2.7.5.7 Fire Station Spill, Elizabeth City, North Carolina

Fuel leaking from an underground pipeline contaminated groundwater with BTEX compounds and MTBE at the "Fire Station Spill Site," located about one-half mile from the US Coast Guard Support Center, in Elizabeth City, North Carolina (USEPA, 1998c). Fuel constituents are estimated to have been in the subsurface less than 10 years. Although no details were provided, field data were apparently used to estimate a first-order rate constant for MTBE degradation. MTBE is apparently degrading under sulfate-reducing and iron-reducing conditions at a rate of 0.0013 day^{-1} (USEPA, 1998c).

Results of the field investigation were evaluated (Wilson *et al*., 1999) using an analytical model of contaminant fate and transport (BIOSCREEN). When the model was calibrated to field data, the calibrated first-order rate constant for MTBE degradation ranged from about 0.0003 day^{-1} to 0.0008 day^{-1} (Wilson *et al*., 1999).

2.7.5.8 Service Station UST Site, Michigan

Coincident BTEX and MTBE plumes were delineated at a service station UST site in Michigan in 1992 (Pavne *et al*., 1997). Groundwater beneath the site was encountered at

a depth of about 10 feet bgs, in glacial till deposits consisting of medium- to fine-grained sands. The plumes were monitored from March 1992 through May 1995. Between March 1992 and May 1994, the plumes appeared to stabilize; and by May 1995, concentrations of BTEX and MTBE in groundwater samples from all monitoring wells were below detection limits. Pavne *et al*. (1997) attribute the disappearance of the plume to "natural attenuation", but do not specify the attenuation mechanism.

2.7.6 Summary

Although only a limited number of field investigations dealing with MTBE have been described in the literature (Table 2.4), the results appear to indicate that degradation of MTBE in the environment does occur, at least under certain circumstances. While MTBE may often be recalcitrant, MTBE degradation has been observed in microcosms and in the field under aerobic conditions (Daniel, 1995; Borden *et al*., 1997), and under anaerobic conditions -- denitrifying (Yeh and Novak, 1994; Borden *et al*., 1997), sulfate-reducing (Yeh and Novak, 1994; Wilson *et al*, 1999), iron-reducing (Borden *et al*., 1997; Landemeyer *et al*., 1998; Wilson *et al*, 1999), and possibly methanogenic (Mormile *et al*., 1994; USEPA, 1998c; Wilson *et al*, 1999). The reported range of first-order rate constants for MTBE degradation, as determined in the field (no degradation to 0.008 day^{-1}) suggest that under some conditions, and at particular sites, biodegradation may be an important mechanism causing the removal of MTBE from the environment. However, the database of field investigations available in the literature remains too limited to allow broad generalizations to be made regarding the conditions that favor MTBE degradation.

2.8 RESULTS OF MULTI-SITE MTBE PLUME STUDIES

The results of multi-site MTBE plume studies have been compiled by Buscheck *et al*., (1998), Happel *et al.* (1998), Mace and Choi (1998), and Rong (1998). In these studies, hydrologic and chemical data from a number of sites were compiled, and analyzed statistically to compare the relative characteristics of BTEX and MTBE plume migration, and to evaluate spatial and temporal trends in the dissolved-phase migration of MTBE.

Time-series chemical data from 29 sites in California and 26 sites in Maryland and other eastern states were analyzed by Buscheck *et al.* (1998). The concentrations of MTBE in the leading edges of plumes at 50 to 65 percent of the sites analyzed were stable or decreasing through time. MTBE concentrations were more likely to increase in downgradient plume locations than were benzene concentrations. This is a probable consequence of the greater mobility of MTBE.

Happel *et al.* (1998) analyzed data from 236 leaking underground fuel tank (LUFT) sites in 24 counties throughout California. These sites were considered representative of the majority of LUFT sites in California based on geologic setting and geographic location. Detectable levels of MTBE in groundwater occurred at 78 percent of the sites, and MTBE was detected in groundwater at 74 percent of the sites at concentrations greater than 5 g/L. The chemical and hydrologic data were sufficient to delineate the lengths of 50 benzene and 50 MTBE plumes; 43 of the 50 sites had coincident plumes. The maximum extent of the MTBE and benzene plumes were determined using cutoff concentrations of 20 g/L and 1 g/L, respectively. The lengths of 90 percent of the MTBE plumes were shorter than 325 feet, while 90 percent of benzene plumes were less than 400 feet in length. The lengths of MTBE and benzene plumes varied significantly. At the 43 sites with coincident MTBE and benzene plumes, the ratio of MTBE plume length to benzene plume length ranged from 0.18 to 3.4.

In addition, groundwater samples were collected from 29 LUFT sites in San Diego County, from 1992 through 1996. The time-series data were analyzed, and it was concluded that:

- Although MTBE and BTEX in groundwater are both typically associated with releases of fuel, and may be present in the same general area, BTEX and MTBE do not usually co-occur in groundwater samples. This may be a result of the disparity in properties between BTEX compounds and MTBE, or may be due to the history of MTBE use. As a consequence, the severity of MTBE contamination cannot be predicted by the degree of TPH or BTEX contamination.

- If BTEX compounds and MTBE each were detected at a particular location, the concentrations of BTEX compounds decreased with time relative to the concentrations of MTBE. This is a consequence of the temporal dissociation of MTBE and BTEX plumes, and may also be a consequence of the more rapid biodegradation of BTEX compounds.

- Chemical data collected over time periods of short duration can significantly underestimate MTBE concentrations. MTBE concentrations were found to increase following precipitation events, sometimes by an order of magnitude.

- Correlation between the concentrations of MTBE and BTEX, and MTBE and TPH in groundwater samples from downgradient wells was poor, probably as a consequence of the fundamental differences in the transport characteristics of MTBE and other hydrocarbon compounds.

- Attenuation of MTBE was not significant compared with attenuation of benzene.

Chemical and time-series concentration data for MTBE and benzene were compiled by Mace and Choi (1998) for 609 LUFT sites in Texas. The geometric mean length of MTBE plumes was 182 feet, and the distal edges of MTBE plumes had moved past the monitoring well network at about 10 percent of sites. MTBE plumes were determined to be, on average, about 27 feet longer than benzene plumes, and were longer than coincident benzene plumes at 56 percent of sites. Analysis of time-series concentration data revealed that the concentrations of MTBE in 83 percent of monitoring wells

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examined were stable, decreasing, or non-detected. This observation suggested that natural attenuation could be an important removal process for MTBE at many sites in Texas.

Rong (1998) evaluated the lengths of MTBE plumes at 51 sites in Los Angeles and Ventura Counties, California, where MTBE concentrations exceeded 10,000 g/L. The average length of an MTBE plume was 125 feet, and approximately 50 percent of the plumes were longer than 100 feet. Over a two-year monitoring period, MTBE concentrations were generally observed to increase in downgradient wells, while the concentrations of benzene and total petroleum hydrocarbons decreased.

SECTION 3

METHODS FOR EVALUATING NATURAL ATTENUATION OF MTBE

The primary objective of a natural attenuation investigation is to evaluate whether natural processes acting on contaminants in the subsurface will reduce contaminant concentrations in groundwater below regulatory or risk-based standards before potential receptor exposure pathways are completed. Consideration of natural attenuation as a potential remedial option also should incorporate a determination of the ability of natural attenuation to meet appropriate Federal and State remediation objectives for a particular site. This requires that a projection be made of the potential extent and concentration of the contaminant plume in time and space. This projection should be based on historical variations in, and the current extent and concentrations of, the contaminant plume, as well as the measured rates of contaminant attenuation.

Because of the inherent uncertainty associated with such predictions, it is the responsibility of the proponent of natural attenuation to provide sufficient evidence to demonstrate that the mechanisms of natural attenuation will reduce contaminant concentrations to acceptable levels before potential receptors are exposed. This requires the use of conservative input parameters and adequate sensitivity analyses so that consideration is given to all plausible contaminant migration scenarios. When possible, both historical data and modeling should be used to provide information that collectively and consistently supports the natural reduction and removal of the dissolved contaminant plume.

The AFCEE document titled *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination*

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Dissolved in Groundwater (AFCEE Technical Protocol, 1995) presents a detailed approach for evaluating the natural attenuation of fuel hydrocarbons. The approach to be followed when evaluating the natural attenuation of MTBE and other fuel oxygenates should mirror that of the AFCEE Technical Protocol (1995) with a few notable additions. These additions are discussed in this section and should be applied on a site-specific basis to supplement the natural attenuation evaluation made using the AFCEE protocols.

A site-specific evaluation of the potential for natural attenuation of MTBE must consider the characteristics peculiar to MTBE including the following:

- MTBE is distributed solely as a constituent of petroleum-based fuels. Therefore, MTBE in the environment will nearly always be associated with other fuel constituents, including BTEX compounds. However, the initial association of MTBE and other fuel-related hydrocarbons in spilled fuel does not mean that MTBE, BTEX compounds, and petroleum hydrocarbons will always be found together in environmental samples. Due to its relatively greater aqueous solubility and greater tendency to partition from soil to groundwater (relative to BTEX constituents), MTBE may migrate more rapidly in the subsurface environment than other fuel constituents. Consequently, MTBE and BTEX plumes may become spatially separated after some period of time.

- MTBE may be the primary fuel constituent at certain locations, comprising up to 15 percent by volume of some gasolines.

- MTBE partitions out of NAPL into the aqueous phase more rapidly than other fuel constituents. Therefore, as spilled petroleum fuel contributes fuel constituents to groundwater, it may eventually become depleted in MTBE even though it continues to function as a source of BTEX compounds and other hydrocarbons.

- The aqueous solubility of MTBE is high (about 50,000 mg/L), and concentrations of MTBE in groundwater near fuel sources are expected to be significant.

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- Because MTBE readily partitions out of NAPL and into the aqueous phase, the concentrations of MTBE in groundwater near a fuel spill may change significantly if the flux of water through the NAPL changes. This is the reason for the increase in MTBE concentrations in groundwater often observed following precipitation events – infiltrating precipitation moves through fuel-contaminated soils and dissolves additional MTBE, which is then transported to the water table. In addition, water-table rises in response to precipitation events may saturate a greater volume of contaminated soil, thereby leaching additional MTBE.

- The vapor pressure of MTBE is relatively high; therefore, MTBE may volatilize from the product phase of a fresh fuel spill. On the other hand, MTBE does not readily volatilize from water. Therefore, volatilization is probably not an important fate mechanism in removing MTBE from groundwater.

- As a consequence of its low organic carbon partition coefficient, MTBE is only slightly sorbed to soil in most hydrogeologic settings, and is virtually unretarded during migration in the aqueous phase. Although MTBE may sorb to soil having relatively elevated organic-carbon content, under most conditions MTBE will migrate in groundwater at approximately the local groundwater seepage velocity, and will generally move more rapidly, and possibly to greater distances from source areas than will other associated fuel constituents (e.g., BTEX).

- Under many (perhaps most) conditions, MTBE appears to be recalcitrant to biodegradation. If biodegradation occurs, detectable concentrations of daughter products (primarily TBA) may be generated. However, because the primary daughter product is also a fuel oxygenate, its appearance with MTBE is not conclusive evidence of MTBE degradation.

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- Detection of MTBE and daughter products in environmental samples may be hindered by elevated detection limits and/or interferences from other compounds (Appendix D). Potential difficulties associated with chemical analyses can be reduced or eliminated by selection of appropriate analytical techniques (e.g., the DAI GC/MS method of Church *et al.* [1997]).

The history and pattern of MTBE use suggests that it will not be present at all fuel-contaminated sites. Because MTBE was generally not used in fuels prior to the late 1970s, and was not widely distributed before the mid-1980s, sites that ceased operations prior to the initiation of the Oxyfuels Program may not be contaminated with MTBE. In addition, because not all States or metropolitan areas participate in the Oxyfuels or RFG Programs, the geographic distribution of MTBE in the United States may be limited. However, as previously noted (Section 2.1), oxygenated gasoline may be distributed in areas that do not participate in the RFG or Oxyfuels Programs. Furthermore, although MTBE is typically considered a gasoline additive, it has also been identified in association with jet fuel, diesel fuel, heating oil, aviation fuel, and waste oil (Kostecki and Leonard, 1998). It therefore seems prudent to suspect MTBE contamination as a possible component of every fuel-hydrocarbon-contaminated site at the initiation of site characterization activities, in the absence of direct evidence to the contrary.

Because of the potentially greater adverse health and environmental effects associated with the BTEX compounds, and because of the current lack of enforceable standards for MTBE in many areas, the BTEX compounds are expected to remain the constituents of primary concern at fuel-affected sites (Happel *et al.*, 1998). Therefore, evaluation and implementation of natural attenuation remedies at fuel-affected sites will be conducted primarily as evaluations of natural attenuation of BTEX compounds and fuel hydrocarbons (AFCEE Technical Protocol, 1995), supplemented, as necessary, by procedures specific to the evaluation of MTBE.

Natural attenuation processes that affect fuel hydrocarbons include non-destructive mechanisms (dispersion, dilution, sorption, volatilization), as well as mechanisms that

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destroy fuel constituents *in situ* (biodegradation). The apparent recalcitrance of MTBE to biodegradation, together with its tendency to remain in the aqueous phase and to move readily with advective groundwater flow, suggest that dispersion may often be the most important attenuation process, acting to reduce the concentrations of MTBE in the subsurface environment. Therefore, evaluation of the distances and times required for dispersion to reduce the concentrations of MTBE to acceptable levels must be a primary objective of MTBE natural-attenuation investigations, in addition to examination of the feasibility of biodegradation.

The remainder of this section describes the steps that should be taken to gather the site-specific data necessary to predict the future extent and persistence of an MTBE plume, with the objective of successfully supporting the natural attenuation option. Subsequent discussion relies on the approach established by existing protocols dealing with fuel hydrocarbons and BTEX compounds (AFCEE Technical Protocol, 1995), but expands certain topics to address concerns specific to MTBE. The flow chart presented as Figure 3.1 (after AFCEE Technical Protocol, 1995) presents the information that must be developed and the important regulatory decision points in the process of implementing natural attenuation.

Predicting the future extent of a contaminant plume requires the quantification of groundwater flow and solute transport and transformation processes, including rates of natural attenuation. Quantification of contaminant migration and attenuation rates, and successful implementation of the natural attenuation option, require completion of the following steps, each of which is outlined in Figure 3.1:

1. Review existing site information;

2. Develop preliminary conceptual model and assess potential for natural attenuation;

3. If MNA is identified as a potentially-appropriate remedy, perform site characterization in support of natural attenuation;

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Review Available
Site Data

Develop Preliminary
Conceptual Model

Make Preliminary
Assessment of Potential
For Risk-Based Remediation
Based on Existing Site
Characterization Data

- Contaminant Type
  and Distribution
- Hydrogeology
- Location of Receptors

Perform Site Investigation
in Support of
Risk-Based Remediation

Refine Conceptual Model and
Complete Pre-Modeling
Calculations

Document Occurrence of
Intrinsic Remediation and
Model Natural Attenuation
Using Numerical Models

Use Results of Modeling and
Site-Specific Information in
an Exposure Assessment

Is There
Unacceptable Risk
To Potential
Receptors ?

NO

YES

Prepare EE/CA In Support
of Natural Attenuation

Evaluate Use of
Other Remedial
Options In
Conjunction With
Natural Attenuation

Free Product
Recovery

Pump
& Treat

Soil Venting

Enhanced
Bioremediation

Bioventing

Air
Sparging

Reactive
Barrier

Assess Potential For
Natural Attenuation
With Remediation
System Installed

Refine Conceptual Model and
Complete Pre-Modeling
Calculations

Model Intrinsic Remediation
Combined with Remedial
Option Selected Above
Using Numerical Models

Use Results of Modeling and
Site-Specific Information in
an Exposure Assessment

Prepare EE/CA Which
Incorporates Appropriate
Risk-Reduction Technologies
and Natural Attenuation

Obtain Regulatory Approval

On Fuel-Contaminated
Sites Only Design,
Construct and Operate
Risk-Reduction Technologies.

Site Point-Of-Compliance
Monitoring Wells and
Finalize Long-Term
Monitoring Plan

If Bioventing or Other
Source Reduction Technologies
are Needed, Operate Those
Systems for 365 days and Then
Resample Soils to Determine
Mass Removal

FIGURE 3.1

**NATURAL ATTENUATION
FLOWCHART**

MTBE Technical Summary Report

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parsons engineering science, inc.
Denver, Colorado

4. Refine conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of natural attenuation;

5. Simulate natural attenuation using analytical or numerical solute fate and transport models that allow incorporation of a biodegradation term, as necessary;

6. Conduct an exposure assessment;

7. If natural attenuation alone is acceptable, prepare LTM plan; and

8. Present findings to regulatory agencies and obtain approval for the natural attenuation option, in conjunction with long-term monitoring.

3.1 REVIEW EXISTING SITE INFORMATION

The first step in the natural attenuation investigation is to review existing site-specific data to determine whether natural attenuation may be a viable remedial option. A thorough review of existing data also allows development of a preliminary conceptual model. The preliminary conceptual model will help identify any shortcomings in the data and will allow placement of additional data collection points in the most scientifically advantageous and cost-effective manner possible.

Available information (e.g., groundwater or soil sampling results from previous investigations) may indicate that MTBE is present at a particular site. In that case, all future investigation activities should be structured to incorporate MTBE into the natural-attenuation evaluation. In addition to evaluating existing physical, geologic, hydrologic, and chemical data available for a site, the investigator concerned with MTBE should attempt to determine the history of MTBE use at that site. Particular attention should be paid to estimating the period of time within which MTBE might first have been used at a site, and the times at which product loss may have occurred. This information is important because the potential migration distance of MTBE in groundwater increases

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with increasing length of time since its introduction to the subsurface. Retail invoices and product inventory records can be useful in evaluating the site-specific history of MTBE.

3.2 DEVELOP PRELIMINARY CONCEPTUAL MODEL AND ASSESS POTENTIAL FOR NATURAL ATTENUATION

After reviewing existing site characterization data, a conceptual model should be developed, and a preliminary assessment of the potential for natural attenuation should be made. The conceptual model is a three-dimensional representation of the groundwater flow and solute transport system based on available geological, biological, geochemical, hydrological, climatological, and analytical data for the site (AFCEE Technical Protocol, 1995). This type of conceptual model differs from the conceptual site exposure models commonly used by risk assessors that qualitatively consider the location of contaminant sources, release mechanisms, transport pathways, exposure points, and receptors. After development, the conceptual model can be used to assist in determining optimal placement of additional data collection points as necessary to aid in the natural attenuation investigation and to develop the solute fate and transport model.

After conceptual model development, an assessment of the potential for natural attenuation must be made. At this point, it may be useful to conduct a screening-level evaluation of the migration potential of MTBE, if MTBE has been identified as a potentially site-related fuel constituent. Such an evaluation may be conducted using estimates of local groundwater flow velocities, and calculating the time required for transport of a conservative constituent to tentatively-identified exposure points. Alternatively, an analytical solution to the advective-dispersive solute transport equation (e.g., van Genuchten and Alves, 1982) could be applied, using the assumption that the constituent of interest (MTBE) was neither degraded nor retarded during dissolved-phase transport. If the results of the screening-level evaluation suggest that MTBE may already have migrated to potential exposure points at concentrations that exceed applicable regulatory guidelines, then natural attenuation may not be a viable option for that site.

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If natural attenuation is determined to be a potentially significant process in contaminant removal or concentration reduction, site characterization activities in support of this remedial option should be completed. If exposure pathways have already been completed and contaminant concentrations exceed regulatory levels, or if such completion is likely, other remedial measures also should be considered. Even so, the collection of data in support of the natural attenuation option can be integrated into a comprehensive remediation plan and may help reduce the cost and duration of other remedial measures such as intensive source removal operations or pump-and-treat technologies.

3.3 PERFORM SITE CHARACTERIZATION IN SUPPORT OF NATURAL ATTENUATION

Detailed site characterization is necessary to document the potential for natural attenuation as discussed in the AFCEE Technical Protocol document (1995). In addition, characterization of the nature and extent of MTBE contamination should address the following considerations:

- The sampling and analytical protocols should incorporate methods appropriate to the sampling and analysis of fuel oxygenates in environmental samples. The analytical methods should be selected to avoid potential problems associated with elevated detection limits and/or interferences from other compounds. Potentially-applicable methods for MTBE, TBA, and TBF in soil and water samples include Method SW8260 and the DAI-GC/MS method of Church *et al*. (1997). Application of these methods is discussed in Appendix D. Suggested analytical protocols to be applied in addition to those presented in the AFCEE Technical Protocol document (1995) for soil and groundwater samples are presented in Table 3.1. Note that samples to be analyzed for fuel oxygenates should not be acidified. Rather, they should be preserved by chilling on ice only, to reduce the possibility of hydrolysis of the oxygenates at low pH, and avoid potential deleterious effects of the mineral acid on the carbowax phase of the GC column.

TABLE 3.1
SOIL AND GROUNDWATER ANALYTICAL PROTOCOLS*
MTBE TECHNICAL SUMMARY REPORT

Matrix	Analysis[a]	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Soil	MTBE, TBA, TBF	GC/MS method SW8260	Handbook method modified for field extraction of soil using methanol	Data are used to determine the extent of soil contamination, the mass of MTBE and daughter products remaining, and the need for source removal	Each soil sampling round	Collect 100 g of soil in a glass container with Teflon-lined cap; cool to 4°C	Fixed-base
Water	MTBE, TBA, TBF	GC/MS method SW8260 or direct-aqueous-injection (DIA) GC/MS method[b] (Church *et al.*, 1997)	Method SW8260 is a handbook method; DIA-GC/MS is a provisional method developed by the US Geological Survey	Method of analysis for MTBE, TBA, and TBF which are among the target analytes for monitoring natural attenuation; MTBE concentrations must also be measured for regulatory compliance	Each sampling round	Collect water samples in a 40 mL VOA vial; cool to 4°C; do not acidify	Fixed-base

[*] These recommended protocols supplement the analytical protocols presented in the AFCEE Technical Protocol (1995).

[a] Standard analyte list for Method SW8260 must be modified to include MTBE, TBA, and TBF.

[b] Preferred method

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- Potential source areas for MTBE are typically associated with fuel storage or distribution facilities (tanks or product-distribution lines). Soil and groundwater samples collected in potential source areas should be analyzed for MTBE. However, because petroleum fuels in source areas may rapidly become depleted in MTBE, and because MTBE is only poorly sorbed to soil, the lack of detectable concentrations of MTBE in samples from source areas does not, of itself, demonstrate that MTBE is not a site-related contaminant. MTBE that originated in source area(s) may have migrated completely out of the area(s), to points downgradient.

MTBE may migrate more rapidly, and to greater distances from source areas, than BTEX compounds or other fuel hydrocarbons. Therefore, soil and/or groundwater sampling points used to characterize the spatial distribution of MTBE may extend to greater distances downgradient than sampling points used to characterize the extent of BTEX constituents. Because Geoprobe® and direct-push sampling points are relatively inexpensive and are rapidly installed, these techniques may be used effectively to initially characterize the location and extent of MTBE contamination in soil and/or groundwater. A typical characterization program might begin with installation of a few sampling points near known or suspected source areas. Sampling points may then be extended at incrementally-increasing distances in the known or inferred downgradient direction(s), until MTBE is no longer detected in samples, or until the maximum probable migration distance from the source(s) estimated during development of the conceptual model (Section 3.2) is reached.

- As a consequence of its relatively rapid migration rate, the maximum extent of MTBE, as established during site characterization activities, may not be an accurate predictor of the maximum extent of MTBE in the future. Consequently, it may be necessary to establish monitoring points at some distance beyond the current extent of MTBE in groundwater, to assist in evaluating its possible future migration, and temporal variations in spatial distribution. Again, a screening-level numerical model

or analytical solution for contaminant transport may be advantageously used to evaluate the need for downgradient monitoring points, and to select their locations.

- Although in many cases MTBE appears to be recalcitrant to biodegradation under field conditions (preceding sections), the results of a limited number of field investigations indicate that, under certain conditions, MTBE may degrade naturally in the environment. The mechanisms of MTBE biodegradation appear to be similar to the mechanisms by which microbial communities degrade other fuel constituents. Therefore, the methods for evaluating the degradation and attenuation of MTBE in the environment also should be similar to current methods for evaluating the degradation and attenuation of BTEX compounds and other fuel constituents (AFCEE Technical Protocol, 1995). To evaluate the site-specific potential for biodegradation of MTBE, groundwater samples should be analyzed for the analytes listed in Table 3.1.

- Because the mechanisms by which MTBE is biodegraded appear to be similar to the mechanisms of BTEX biodegradation, distinguishing MTBE degradation from degradation of other fuel hydrocarbons using only geochemical parameters (nitrate, sulfate, iron, methane, ORP) may be difficult. However, unlike other fuel constituents, biodegradation of MTBE can produce detectable concentrations of daughter products, in particular TBA. TBA may degrade more slowly than MTBE (Suflita and Mormile, 1993; Salanitro *et al*., 1994), and consequently may accumulate in the environment. If MTBE is potentially a site-related contaminant, environmental samples also should be analyzed for daughter products of MTBE degradation (TBA and TBF). In order to achieve the low detection limits necessary for the analysis of potential degradation daughter products, the DIA-GC/MS method (Church *et al*., 1997) should be used (Table 3.1 and Appendix D). TBA is also used as a fuel oxygenate, so that its detection at a site in association with MTBE is not conclusive evidence of MTBE biodegradation. However, the distribution and concentrations of MTBE and TBA should be examined to evaluate

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whether stoichiometric increases in the concentrations of TBA are spatially or temporally associated with decreasing concentrations of MTBE.

Several non-destructive processes, including dilution, sorption, and hydrodynamic dispersion, can cause reductions in contaminant concentrations and an apparent reduction in the total mass of contaminant in a system. In order to distinguish the mass of contaminant actually removed from the system (degraded) from diluted, sorbed, or dispersed mass, it is necessary to correct observed concentrations for the effects of these processes. This is done by incorporating independent assessments of these processes into the comprehensive solute transport model. These processes are described in detail in other documents (e.g., AFCEE Technical Protocol, 1995). Example calculations are presented in Appendix E.

The biodegradation of compounds that are retarded during migration (e.g., BTEX) can be estimated by normalizing the measured concentration of the compound to the concentration of a tracer that is at least as sorptive as the chemical of interest, but which is biologically recalcitrant (AFCEE Technical Protocol, 1995). For compounds that may be recalcitrant, and are not readily sorbed to the aquifer matrix (e.g., MTBE), techniques that can be applied to correct for apparent mass loss include (Appendix E):

- Regression of chemical concentration versus travel distance or travel time from the chemical source (Buscheck and Alcantar, 1995),

- Evaluation of changes in mass flux through a given volume of the aquifer (Daniel, 1995; Borden *et al*., 1997); and

- Comparison of estimated total constituent mass remaining in groundwater with the estimated total constituent mass in the original spill (Barker *et al*., 1998).

The latter two methods generally require more detailed site characterization and/or knowledge of the site history than does normalization to an unreactive tracer, and are difficult, at best, to apply (Barker *et al*., 1998). The method of Buscheck and Alcantar

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(1995) requires that the longitudinal dispersion of a contaminant plume be estimated, so that the effects of concentration reduction resulting from dispersion can be accounted for in estimating the rate of biodegradation. However, as previously noted, dispersion may be the most important mechanism, causing reductions in MTBE concentrations downgradient from source areas. Therefore, it may be necessary to quantitatively estimate a site-specific value for longitudinal dispersion, using a conservative tracer (e.g., bromide or chloride; Freeze and Cherry, 1979; Domenico and Schwartz, 1998) prior to applying the method of Buscheck and Alcantar (1995).

As an alternative, microcosm studies using site-specific aquifer materials and contaminants can be used to demonstrate that the microorganisms necessary for biodegradation of MTBE are present and active, and can be used as direct evidence to evaluate natural attenuation. In the case of MTBE degradation, which can be difficult to document at the field scale, microcosm investigations, if properly designed, implemented, and interpreted, may provide the most convincing evidence of the occurrence of intrinsic bioremediation. Such studies are the only "line of evidence" that allows an unequivocal mass balance of the biodegradation of environmental contaminants.

Microcosms are most appropriately used as indicators of the potential for intrinsic bioremediation, and to prove that losses are biological, but biodegradation rate constants determined by microcosm studies often are much greater than rates achieved in the field. The preferable method of determining biodegradation rate constants is by *in-situ* field measurement, although, as noted, this may not be possible for MTBE. Procedures that can be used to collect material for microcosm studies, set up and analyze the microcosm(s), and to interpret the results of the studies are described in detail in other documents (e.g., AFCEE Technical Protocol, 1995).

3.4 REFINE CONCEPTUAL MODEL, COMPLETE PRE-MODELING CALCULATIONS, AND DOCUMENT INDICATORS OF NATURAL ATTENUATION

Site investigation data are used to refine the conceptual model and calculate rates of groundwater flow, sorption, dilution, and biodegradation. The results of these calculations are used to scientifically document the occurrence and rates of natural attenuation and to assist in subsequent simulations of natural attenuation through time. This procedure is described in detail in the AFCEE Technical Protocol (1995).

3.5 SIMULATE NATURAL ATTENUATION USING SOLUTE FATE AND TRANSPORT MODELS

Simulation of contaminant fate and transport enables predictions to be made of the migration and attenuation of the contaminant plume over time. Modeling is a tool that allows site-specific information to be used to evaluate the migration and attenuation of solutes under governing physical, chemical, and biological processes, as constrained by specified initial and boundary conditions. However, the results of the modeling effort are not in themselves sufficient proof that natural attenuation is occurring at a given site, and must be supported with field data – in particular, chemical concentration data collected through time at several monitoring locations. Model simulations and predictive results are only as good as the original data provided as input to the model; therefore, an investment in thorough site characterization will improve the defensibility of the modeling results. This is particularly important in the case of fuel hydrocarbon plumes containing MTBE, which tends to migrate more rapidly than other hydrocarbon compounds.

Several well-documented and widely accepted solute fate and transport models are available for simulating the fate and transport of fuel hydrocarbons under the influence of advection, dispersion, sorption, and biodegradation. In the case of MTBE, application of a transport model may be particularly useful in distinguishing observed reductions in concentrations due to hydrodynamic dispersion from the effects of biodegradation. The use of solute fate and transport modeling in natural-attenuation evaluations is described in detail in other documents (AFCEE Technical Protocol, 1995).

3.6 PREPARE LONG-TERM MONITORING PLAN

Preparation of a LTM plan consists of identifying appropriate locations for groundwater monitoring wells, and developing a groundwater sampling and analysis strategy. Long-term monitoring is used to monitor spatial and temporal variations in the configuration of the plume, and to verify that natural attenuation is occurring at rates sufficient to protect potential downgradient receptors. The LTM plan should be developed based on site characterization data, the results of solute fate and transport modeling, and the results of the exposure pathways analysis. The results of the solute fate and transport model can be used to assist in identifying locations for LTM wells.

For sites affected by MTBE, the dimensions of the monitoring network, and locations of monitoring wells, should be adjusted to account for the transport characteristics of MTBE. MTBE is more mobile (less retarded) than BTEX compounds, and is considerably more soluble, so that MTBE tends to migrate farther, and more rapidly, than BTEX compounds (on average, about 40 percent further, at detectable concentrations; Mace and Choi, 1998). Furthermore, because MTBE readily partitions out of the fuel phase and into water, the source of MTBE (fuel spill) is typically more rapidly depleted of MTBE than of BTEX.

In order to evaluate the concentrations of fuel constituents and temporal changes in geochemical conditions, selected groundwater samples should be analyzed for BTEX, MTBE, and potential degradation daughter compounds (in particular, TBA), dissolved oxygen, nitrate, iron (II), sulfate, and methane. Sampling frequency should be evaluated on a site-by-site basis. However, because the concentrations of MTBE in groundwater near source areas are known to fluctuate significantly in response to precipitation events (Happel *et al*., 1998), schedules for monitoring MTBE in groundwater should remain flexible. For example, in areas having distinct wet and dry seasons, the monitoring schedule may be adjusted to allow most monitoring events to be completed during the wet season, or following significant precipitation events.

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Other factors to be considered in locating and constructing monitoring wells, and developing LTM protocols, are discussed in other documents (AFCEE Technical Protocol, 1995).

3.7 REGULATORY CONSIDERATIONS

Section 2.3 discusses current regulatory standards. Although there are no Federally-enforceable standards, many states are promulgating regulatory standards based on the Federal guidelines of 20 to 40 g/L in drinking water. The purpose of regulatory negotiations is to provide scientific documentation that supports natural attenuation as the most appropriate remedial option for a given site. All available site-specific data and information developed during the site characterization, conceptual model development, pre-modeling calculations, biodegradation rate calculation, groundwater modeling, model documentation, and LTM plan preparation phases of the natural attenuation investigation should be presented in a consistent and complementary manner during negotiations. Convincing evidence that natural attenuation is occurring at rates sufficient meet regulatory compliance levels at the point-of-compliance, and to protect human health and the environment will be of particular interest to regulatory personnel. Although the current environmental regulatory framework favors attenuation mechanisms that destroy chemicals *in-situ* (e.g., biodegradation), mechanisms that result in concentration reduction without chemical destruction (e.g., dilution and dispersion) are not *a priori* ruled out. Therefore, regulators must be presented with a "weight of evidence" argument in support of this remedial option. For this reason, all available evidence in support of natural attenuation must be presented at the regulatory negotiations.

SECTION 4

CONCLUSIONS AND RECOMMENDATIONS

This technical report documents the physical and chemical characteristics of the fuel oxygenate MTBE that influence its movement and fate in the environment, summarizes the literature regarding the results of field-scale and laboratory evaluation of the degradation of MTBE, and provides recommendations for data collection and analysis in support of natural attenuation supplemented with LTM for restoration of groundwater contaminated with MTBE.

Although only a limited number of field investigations dealing with MTBE have been described in the literature, the results indicate that in some circumstances, degradation of MTBE in the environment does occur. While MTBE may often be recalcitrant, MTBE degradation has been observed in microcosms and in the field under aerobic and anaerobic conditions. The reported range of first-order rate constants for MTBE degradation, as determined in the field (no degradation to 0.008 day^{-1}) suggest that under some conditions, biodegradation may be an important mechanism causing the removal of MTBE from the environment. However, the database of field investigations available in the literature remains too limited to allow broad generalizations to be made regarding the conditions that favor MTBE degradation.

The following significant observations, conclusions, and recommendations are derived from the existing body of technical literature regarding the properties, occurrence, movement, and fate of MTBE in the environment:

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- MTBE exists solely a constituent of petroleum-based fuels, and will typically be introduced to the environment as a consequence of product loss. Groundwater contamination by MTBE has been associated with gasoline, diesel fuel, jet fuel, heating oil, aviation fuel, and waste oil. Therefore, MTBE in the environment will nearly always be associated with other fuel constituents.

- MTBE may be the primary fuel constituent at certain locations, comprising up to 15 percent by volume of some gasolines.

- Detectable concentrations of MTBE in air can produce detectable concentrations of MTBE in precipitation. Therefore, precipitation falling near sources of vapor-phase MTBE will probably contain detectable concentrations of MTBE. If MTBE in precipitation migrates in the dissolved phase to the water table, increased levels of MTBE in nearby groundwater may result.

- MTBE partitions out of NAPL into the aqueous phase more readily than BTEX or other fuel constituents. Therefore, as spilled petroleum fuel contributes fuel constituents to groundwater, it may rapidly become depleted of MTBE even though it continues to function as a source of BTEX compounds and other hydrocarbons.

- Because MTBE readily partitions out of NAPL and into the aqueous phase, the concentrations of MTBE in groundwater near a fuel spill may change significantly if the flux of water through the NAPL changes.

- In most hydrogeologic settings, MTBE is only slightly sorbed to soil and is only slightly retarded during migration in the aqueous phase. Although MTBE may sorb to soil containing high concentrations of organic carbon, under most circumstances, MTBE will migrate in groundwater at approximately the local groundwater seepage velocity, and will generally move more rapidly, and possibly to greater distances from source areas, than will other fuel constituents. Soil and/or groundwater sampling points used to characterize the spatial distribution of MTBE may extend to greater distances downgradient than sampling points used to characterize the extent of BTEX constituents. As a consequence of its relatively rapid migration rate, as compared with BTEX constituents, the maximum extent of MTBE, as established during site characterization activities, may not be an accurate predictor of the maximum extent of MTBE in the future. Consequently, it may be necessary to establish monitoring points some distance beyond the current extent of MTBE in groundwater to assist in evaluating its possible future migration.

- At the field scale, dispersion may be the most important process, acting to reduce the concentrations of MTBE in groundwater downgradient from source areas.

- The mechanisms of MTBE biodegradation appear to be similar to the mechanisms by which microbial communities degrade other fuel constituents, and methods for evaluating the degradation and attenuation of MTBE in the environment are similar to current methods for evaluating the degradation and attenuation of BTEX compounds and other fuel constituents. However, distinguishing MTBE degradation from degradation of other fuel hydrocarbons using only geochemical parameters may be difficult. If biodegradation occurs, detectable concentrations of daughter products (primarily TBA) may be generated. However, because the primary daughter product also is a fuel oxygenate, its appearance with MTBE is not conclusive evidence of MTBE degradation.

- The sampling and analytical protocols used should incorporate methods appropriate to the sampling and analysis of fuel oxygenates in environmental samples, including Method SW8260 and the method of Church *et al*. (1997).

- Samples collected at field sites where MTBE is known or suspected to be constituent of potential concern should be analyzed for MTBE degradation products (TBA and TBF), as well as for MTBE. The results obtained can assist in documenting the biodgradation (or lack thereof) of MTBE at the field scale, and can, in the future, supplement the existing database regarding MTBE fate and transport.

- In order to distinguish the mass of contaminant actually removed from the system (degraded) from diluted, sorbed, or dispersed mass, MTBE concentrations observed in the field must be corrected for the effects of these processes. Therefore, quantification of environmental factors governing contaminant sorption and migration (e.g., groundwater flow velocity and aquifer dispersivity) will probably be necessary.

- Because MTBE degradation is difficult to document at the field scale, microcosm investigations may provide the most convincing evidence of the occurrence of intrinsic bioremediation of MTBE.

SECTION 5

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USEPA. 1998b. *MTBE Fact Sheet #3 Use and Distribution of MTBE and Ethanol..,* USEPA Office of Underground Storage Tanks. Washington, D.C. EPA-510-F-97-016. 3 pp. January.

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Zogorski, J.S., A. Morduchowitz, A.L. Baehr, B.J. Bauman, D.L. Conrad, R.T. Drew, N.E. Korte, W.W. Lapham, J.F. Pankow, and E.R. Washington. 1997. *Fuel Oxygenates and Water Quality: Current Understanding of Sources, Occurrence in*

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Zogorski, J.S., G.C. Delzer, D.A. Bender, P.J. Squillace, T.J. Lopes, A.L. Baehr, P.E. Stackelberg, J.E. Landmeyer, C.J. Boughton, M.S. Lico, J.F. Pankow, R.L. Johnson, and N.R. Thomson. 1998. MTBE: Summary of findings and research by the U.S. Geological Survey, *In* 1998 Annual Conference of Water Quality, Atlanta, Ga. [Proceedings]: American Water Works Association (in press).

APPENDIX A

ANNOTATED BIBLIOGRAPHYOF MTBE REFERENCES

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American Petroleum Institute

American Petroleum Institute, 1997. Field studies of BTEX and MTBE intrinsic bioremediation: Washington, D.C., Health and Sciences Department, American Petroleum Institute Publication No. 4654, 241 p.

A UST release site in Sampson County, N.C. was studied. The site was instrumented with more than 50 observation wells that were monitored for several years. Companion laboratory and modeling studies were conducted to facilitate interpretation of the field data. Effective first order decay rates varied from 0 to 0.0010 d^{-1} for MTBE. Laboratory microcosm studies confirmed MTBE biodegradation under aerobic conditions; however the extent of biodegradation was limited. BIOPLUME II and a 3-D analytical model were evaluated for their ability to simulate the transport and biodegradation of MTBE and BTEX at the site. Neither model could accurately simulate contaminate concentrations throughout the length of the plume.

American Petroleum Institute

American Petroleum Institute, 1998. Delineation and characterization of the Borden MTBE plume--An evaluation of eight years of natural attenuation processes: Washington, D.C., Health and Sciences Department, American Petroleum Institute Publication No. 4668, 87 p.

Baehr, A.L., R.J. Baker, M.A. Lahvis

Baehr, A.L., R.J. Baker, and M.A. Lahvis, 1997. Transport of methyl *tert*-butyl ether across the water table to the unsaturated zone at a gasoline-spill site in Beaufort, S.C., *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, pp. 417-418.

Evaluation of gaseous phase MTBE and BTEX was made in the unsaturated zone above the water table where high concentrations of these contaminates were located. Measured gaseous-phase concentrations of both BTEX and MTBE above the water table decline more sharply than predicted on the basis of transport if no reactions are assumed to occur. For BTEX the difference is attributed to aerobic degradation in the unsaturated zone. For MTBE, the difference is smaller that that for BTEX, but is significant enough to suggest that aerobic degradation of MTBE may

occur in the unsaturated zone. Such degradation enhances transport across the water table because diffusive flux is proportional to the concentration gradient. The observation of aerobic degradation just above the water table also implies that MTBE may degrade in parts of the groundwater plume where dissolved oxygen is present.

Baehr, A.L., P.E. Stackelberg, R.J. Baker, L.J. Kauffman, J.A. Hopple, M.A. Ayers

Baehr, A.L., P.E. Stackelberg, R.J. Baker, L.J. Kauffman, J.A. Hopple, M.A. Ayers, 1997. Design of a sampling network to determine the occurrence and movement of methyl *tert*-butyl ether and other organic compounds through the urban hydrologic cycle, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, pp. 400-401.

Data is currently being collected in southern New Jersey to document the occurrence and identify the processes that affect MTBE transport in various parts of the hydrologic cycle. Rationale for the design of the study is presented and the use of mathematical models to calculate rates of movement through the hydrologic cycle are outlined.

Barker, J.F., C.E. Hubbard, L.A. Lemon

Barker, J.F., C.E. Hubbard, L.A. Lemon, 1990. The influence of methanol and MTBE on the fate and persistence of monoaromatic hydrocarbons in groundwater: Ground Water Management, v. 4, pp. 113-127.

A natural gradient tracer injection experiment has been performed at CFB Borden, Ontario to investigate the influence of methanol and MTBE on the behavior of monoaromatic hydrocarbons in groundwater. Three slugs of gasoline-contacted groundwater were injected into a shallow, aerobic sand aquifer and allowed to migrate in the natural flow system. The initial concentrations of solutes represented those expected from spills of gasoline containing: 1) 85% methanol, 2) 15% MTBE, 3) no additives. Chloride was injected with each plume as a conservative tracer. Solute distributions were monitored over 16 months by periodic sampling of a dense network of multilevel piezometers.

A preliminary analysis of the data indicates that both methanol and MTBE have migrated at about the same rate as the conservative tracer. Neither oxygenate had a discernible effect on the rate of migration of the monoaromatics. Methanol significantly slowed the rate of disappearance of several monoaromatics, while MTBE had no such effect. The methanol itself was essentially removed within 476 days. The MTBE was recalcitrant. Laboratory microcosm experiments performed in conjunction with the field study provide data that is generally consistent with the field observations.

Barker, J.F., M. Schirmer, C.E. Hubbard

Barker, J.F., M. Schirmer, C.E. Hubbard, 1996. The longer term fate of MTBE in the Borden Aquifer, *in* Stanley, Anita, ed., NWWA/API Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation Conference, Houston, Tex., Nov. 13-15, 1996, [Proceedings]: Houston, Tex., National Water Well Association and American Petroleum Institute, pp. 5-14.

Barker, J.F., M. Schirmer, B.J. Butler, C.D. Church

Barker, J.F., M. Schirmer, B.J. Butler, C.D. Church, 1998. Fate and transport of MTBE in groundwater - results of a controlled field experiment in light of other experience, *in* The Southwest Focused Ground Water Conference--Discussing the Issue of MTBE and Perchlorate in Ground Water, Anaheim, Calif., June 3-4, 1998, [Proceedings]: Anaheim, Calif., National Ground Water Association, pp. 10-14.

A natural gradient test was performed in the shallow, aerobic sand aquifer at Canadian Forces Base (CFB) Borden in 1988. Groundwater containing MTBE and petroleum-derived hydrocarbons was injected below the water table along with chloride (Cl^-) as a conservative tracer. The mass of BTEX compounds in the plume diminished significantly over 474 days due to aerobic biodegradation. MTBE showed perhaps a small decrease in mass. In 1995/96, ground water sampling was undertaken to define the mass of MTBE still present in the aquifer. Only 3% of the original MTBE mass was found. Sorption, volatilization, abiotic degradation, and plant uptake were ruled out as significant attenuation processes. A microcosm experiment provided some suggestion that the aerobic biodegradation may have played a major role in the attenuation of MTBE within the Borden aquifer.

Dispersion alone is unlikely to provide sufficient natural attenuation for MTBE. Slow MTBE biodegradation, while difficult to substantiate, may provide sufficient natural attenuation for same MTBE impacted groundwaters. This uncertainty about MTBE fate in groundwater will mean that remediation using monitored natural attenuation will require substantial ongoing monitoring to demonstrate attainment of remedial goals.

Barreto, R.D., K.A. Gray, K. Anders

Barreto, R.D., K.A. Gray, K. Anders, 1995. Photocatalytic degradation of methyl-*tert*-butyl ether in TiO_2 slurries--a proposed reaction scheme: Water Resources, v. 29, no. 5, pp. 1243-1248.

Although MTBE is difficult to treat economically with conventional techniques, it has been found to be readily degraded photocatalytically. In Batch TiO_2 slurries and under the experimental conditions used in these experiments MTBE degradation proceeded with an initial pseudo first-

order rate constant of $1.2 \times 10^{-3}\,s^{-1}$. The primary by-products of this reaction have been identified as t-butyl formate and t-butyl alcohol, both of which are also readily degraded photocatalytically, albeit at slightly slower rates that MTBE. Mass balance calculations have shown that MTBE is virtually completely mineralized and a reaction scheme is proposed.

Bass, D.

Bass, D., 1996. A Review of Treatment Technologies for MTBE [abs.], *in* Society of Environmental Toxicology and Chemistry abstract book, 17th, Washington, D.C., November 17-21, 1996: Washington, D.C., SETAC, p. 311.

Available treatment technologies for MTBE contamination in soil, groundwater, and recovered groundwater are reviewed and assessed. MTBE is more soluble and more mobile in groundwater that most hydrocarbons, so it is usually the first gasoline constituent to reach sensitive receptors. Treatment of MTBE is complicated by its Henry's constant, which is lower than most other gasoline constituents. Furthermore, evidence of biodegradability of MTBE is mixed, and MTBE does not degrade rapidly abiotically. Groundwater pumping is usually employed to contain and collect MTBE-contaminated groundwater, often successfully because of its high aqueous solubility. Air sparging/soil vapor extraction is also successfully employed to treat MTBE, but its effectiveness is reduced by the low Henry's constant of MTBE. Sparging and other aerobic bioremediation approaches are hampered by the poor biodegradability of MTBE. Oxidation technologies, such as ozone injection, hold promise for rapid *in situ* remediation of MTBE. Treatment of recovered groundwater contaminated with MTBE is also problematic. MTBE adsorbs poorly to granular activated carbon; advanced oxidation processes are effective on MTBE, but entail high capital and operation costs; bioreactors are of questionable effectiveness on MTBE. Air stripping is usually the most cost-effective treatment technology for MTBE so long as the off gas from the air stripper can be discharged without treatment. However, off gas treatment is expensive, so groundwater is sometimes heated to reduce the requirement for stripping air.

Beckenbach, E.H., and Happel, A.M.

Beckenbach, E.H., and Happel, A.M., 1998. Methyl tertiary butyl ether plume evolution at California LUFT sites, *in* The Southwest Focused Ground Water Conference-- Discussing the Issue of MTBE and Perchlorate in Ground Water, Anaheim, Calif., June 3-4, 1998, [Proceedings]: Anaheim, Calif., National Ground Water Association, p. 15.

MTBE has been detected at approximately 80% of California leaking underground fuel tank (LUFT) sites previously studied by Lawrence Livermore National Laboratory. Furthermore, at 63 % of these sites concentrations exceeded the proposed EPA health advisory of 70 ppb. Since MTBE is thought to be recalcitrant and highly soluble in water and has only recently been used in

large quantities to comply with statewide reformulated gasoline requirements, there is significant interest in the temporal evolution of MTBE plumes in groundwater. In particular, we are interested determining if observed concentration and the issues we are collecting and analyzing time series data from LUFT sites throughout California make available by request from major petroleum distributions. Analysis includes the production of joint probabilistic distributions of observed MTBE concentrations as functions of distance from source location and time as well as distributions of estimated plume length estimates are evaluated to predict potential future impacts to groundwater resources. Traditionally, benzene has been considered the contaminant of concern at LUFT sites due to its relatively high solubility and carcinogenic potency. However, the extent of benzene migration is believed to often be limited by biodegradation in groundwater. Parallel analysis of benzene and MTBE plume evolution is presented to compare known and potential impacts resulting from historical releases of the non-conservative contaminant benzene, and recent releases of the potentially recalcitrant contaminate MTBE.

Bolton, J.R., A. Safarzadeh-Amiri, S.R. Cater, B. Dussert, M.I. Stefan, J. Mack

Bolton, J.R., A. Safarzadeh-Amiri, S.R. Cater, B. Dussert, M.I. Stefan, J. Mack, 1998. Mechanism and efficiency of the degradation of MTBE in contaminated groundwater by the UV/H_2O_2 Process, *in* The Southwest Focused Ground Water Conference--Discussing the Issue of MTBE and Perchlorate in Ground Water, Anaheim, Calif., June 3-4, 1998, [Proceedings]: Anaheim, Calif., National Ground Water Association, pp. 36-39.

Advanced oxidation processes (AOPs), such as UV/H_2O_2 and ozone/H_2O_2, are promising and appear to offer the least cost and most practical option of remediating MTBE from groundwater. Ozone/H_2O_2 is widely used in Europe for the removal of pesticides from drinking water. However, the use of ozone-based AOPs may be limited in bromide ion-bearing waters, due to the formation of the undesirable bromate ion, a suspected carcinogen.

The UV/H_2O_2 process involves the photolysis of added H_2O_2 to generate hydroxyl radicals (.OH), which then attack and oxidize (with the aid of dissolved O_2) organic pollutants converting them eventually to CO_2 and H_2O. This process has been used routinely for groundwater remediation in over 200 sites worldwide. Its main advantage over ozone-based processes is that it does not form bromate ion.

This paper discusses the degradation of MTBE in tap water by the UV/ H_2O_2 process from the standpoint of its efficiency. Intermediate oxidation by-products have been identified and quantified, and their relevance to the water industry is discussed.

Borden, R.C.

Borden, R.C., 1997. Intrinsic bioremediation of MTBE and BTEX--Field and laboratory results, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 426-427.

An extensive field and laboratory study was conducted at an UST release in Sampson County, NC, to improve our understanding of those factors limiting intrinsic bioremediation of dissolved gasoline components in groundwater. Field-scale first-order decay rates for MTBE and BTEX were estimated using a mass flux approach that does not require fitting a solute transport model to concentrations at individual wells. The field monitoring result show evidence of MTBE decay near the contaminate source. However, there is no evidence for MTBE decay in the downgradient aquifer.

Borden, R.C., R.A. Daniel, L.E. LeBrun IV, C.W. Davis

Borden, R.C., R.A. Daniel, L.E. LeBrun IV, C.W. Davis, 1997. Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer: Water Resources Research, v. 33, no. 5, pp. 1105-1115.

Three-dimensional field monitoring of a gasoline plume showed rapid decay of toluene and ethylbenzene during downgradient transport with slower decay of xylenes, benzene, and MTBE under mixed aerobic-denitrifying conditions. Decay was most rapid near the source but slower farther downgradient. Effective first-order decay coefficients varied from 0 to 0.0010 d^{-1} for MTBE, from 0.0006 to 0.0014 d^{-1} for benzene, from 0.0005 to 0.0063 d^{-1} for toluene, from 0.0008 to 0.0058 d^{-1} for ethylbenzene, from 0.0012 to 0.0035 d^{-1} for m-, p-xylene, and from 0.0007 to 0.0017 d^{-1} for o-xylene. Laboratory microcosm studies confirmed MTBE biodegradation under aerobic conditions; however, the extent of biodegradation was limited.

Brown, A., J.R.C. Farrow, R.A. Rodriquez, B.J. Johnson, A.J. Bellomo

Brown, A., J.R.C. Farrow, R.A. Rodriquez, B.J. Johnson, A.J. Bellomo, 1997. Methyl tertiary butyl ether (MTBE) contamination of the city of Santa Monica drinking water supply, *in* Stanley, Anita, ed., NWWA/API Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation Conference, Houston, Tex., Nov. 12-14, [Proceedings]: Houston, Tex., National Water Well Association and American Petroleum Institute, pp. 35-59.

This is a summary of the investigation of MTBE contamination of two well fields used for drinking water supply for the City of Santa Monica. The objectives of the investigation were as follows:

- Review available data on the production, use, chemical characteristics, fate and transport, toxicology, and remediation of MTBE;

- Identify locations of potential sources of MTBE groundwater contamination at the well fields;

- Develop an understanding of the hydrologic pathways from the potential sources to the drinking water wells; and

- Evaluate alternative treatment technologies for the removal of MTBE from drinking water.

A field program was conducted at the major well filed, including soil gas surveys, CPTs, soils borings and well installations, geophysics, and aquifer testing. The field program provided site data, which allowed the conceptual hydrogeologic model to be refitted to actual site conditions. A preliminary groundwater flow model, based upon the revised conceptual model, was then developed to evaluate the possible migration pathways from possible source sites to the impacted well field.

Bruce, C.L., C.D. Gilbert, R.L. Johnson, P.C. Johnson

Bruce, C.L., C.D. Gilbert, R.L. Johnson, P.C. Johnson, 1998. Methyl Tert-Butyl Ether Removal by In Situ Air Sparging in Physical Model Studies: The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998, Proceedings: Columbus, Ohio, Battelle Press, pp.293-298.

Two-dimensional laboratory-scale physical aquifer model studies at Arizona State University and Oregon Graduate Institute have been conducted to simulate MTBE removal by air sparging. Results for saturated media experiments indicate that approximately 85% of immiscible-phase MTBE can be removed from MTBE-containing test mixtures by volatilization under idealized conditions. These experiments also suggest that MTBE removal efficiency by volatilization is affected by the degree of media saturation

Buscheck, T.E., D.J. Gallagher, T.R. Peargin, D.L. Kuehne, C.R. Zuspan

Buscheck, T.E., D.J. Gallagher, T.R. Peargin, D.L. Kuehne, C.R. Zuspan, 1998. Occurrence and behavior of MTBE in groundwater, *in* The Southwest Focused Ground Water Conference-- Discussing the Issue of MTBE and Perchlorate in Ground Water, Anaheim, Calif., June 3-4, 1998, [Proceedings]: Anaheim, Calif., National Ground Water Association, pp. 2-3.

Groundwater analytical data for more than 700 service station sites nationwide where groundwater was analyzed for MTBE were examined for this study. MTBE was detected at

approximately 80% of the investigated sites. MTBE was detected at 88% of operating sites, and at 74% of non-operating sites. The frequency of MTBE occurrence at non-operating sites is less than that at operating sites, because some of the service stations were closed prior to its use in gasoline. The detection frequency at operating sites in California (83%) is slightly less than in Texas (96%) and Maryland (98%). Later introduction of MTBE in California, coupled with early facility upgrades, required by the 1998 regulations, may contribute to the lower detection frequency in this state. Maximum MTBE concentrations also vary across the country, due to hydrogeologic conditions and the timing of MTBE introduction and composition in gasoline. MTBE concentrations exceeded 1 mg/L at 47% of 251 operating sites in California, 63% of 153 Texas sites and 82% of 41 Maryland sites.

Time series data were available for 29 Southern California sites and 26 sites from Maryland and other Eastern states. These data were evaluated to determine concentrations versus time trends for monitoring wells at the downgradient edge of the plume. Time series data suggest 50% to 65% of the sites have stable or decreasing MTBE concentration trends at the leading edge of the plume. MTBE concentrations are more likely to increase than benzene at the downgradient edge of the plume, consistent with the known chemical properties of these compounds. However, the highest MTBE concentrations are typically found near the source.

Time series data were used to compare groundwater remediation rates for MTBE, benzene, and xylene for eight Maryland sites. Remediation systems were combined vapor extraction and groundwater extraction. The database included 84 monitoring wells located with in the source area. Pre-remediation time series data indicate that years after the release, MTBE remains in the residual NAPL. The regression of concentration versus time during remediation yielded very similar decay rates for the three compounds (varying between 0.34 and 0.39% per day). Dissolution and volatilization of MTBE does not occur as rapidly as would have been calculated. However, groundwater remediation was effective, with average concentration reduction of 95% for MTBE, 94% for benzene, and 92% for xylene. These data also suggest air-based remediation systems can be effective years after the release occurred.

Butillo, J.V., A.D. Pulido, N.M. Reese, M.A. Lowe

Butillo, J.V., A.D. Pulido, N.M. Reese, M.A. Lowe, 1994. Removal Efficiency of MTBE in Water: Confirmation of a Predictive Model through Applied Technology, *in* Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection and Remediation: National Ground Water Association, Dublin, Ohio, pp. 91-105.

Remedial technologies were evaluated for the treatment of MTBE in water from petroleum storage facilities. Air (AS) packed column heights were compared to air stripping at elevated

temperatures. This was done to evaluate the effectiveness of raising the influent water temperature to increase stripping efficiency. The performance criteria were based on an influent concentration of 4300 ppm of MTBE removal efficiencies: 99.41%, 99.78% and 100.00% at temperatures or 65% $^\circ$F, 80°F, and 100°F, respectively. The model assumed a 30-foot packed column height with an airflow rate of 3000 actual cubic feet per minute (acfm).

In comparing packed column height performance, the model assumed an ambient influent water temperature of 50°F. The model predicted removal efficiencies as a function of column height were as follows: 96.00%, 99.42%, and 99.78% at packed column heights of 30, 50 and 60 feet, respectively.

The engineering design of a water treatment system utilized the model prediction of raising the influent water temperature to increase removal efficiency of MTBE. A 30-ft. packed column AS with thermal oxidation off-gas treatment was incorporated into the existing water treatment system. A heat exchanger in the oxidizer exhaust stack was utilized to heat the AS influent water stream to 80°F. Laboratory analytical results of effluent water samples indicate a removal efficiency of 99.98% for MTBE and BTEX from the water system. The system performance achieved results comparable with the model predictions. These results indicate that increasing water temperatures increases the removal efficiency of these organic compounds for the water stream. Economic evaluations show that, where applicable, this design provided a more cost-effective method for water treatment in comparison to conventional technologies.

Buxton, H.T., J.E. Landmeyer, A.L. Baehr, C.D. Church, P.G. Tratnyek

Buxton, H.T., J.E. Landmeyer, A.L. Baehr, C.D. Church, P.G. Tratnyek, 1997. Interdisciplinary investigation of subsurface contaminant transport and fate at point-source releases of gasoline containing MTBE, *in* Stanley, Anita, ed.: NWWA/API Petroleum Hydrocarbon Conference--Prevention, Detection, and Restoration, Houston, Tex., Nov. 12-14, 1997, [Proceedings]: Houston, Tex., National Water Well Association and American Petroleum Institute, pp. 2-18.

An investigation of the fate and transport of MTBE from point-source gasoline releases is being conducted by intensive characterization of a field site in Beaufort, SC. The objective of the investigation is to evaluate the potential for natural attenuation of MTBE compared to BTEX by dilution from mixing, adsorption, biotic and abiotic transformation, and volatilization. Preliminary results indicate a decrease in aqueous BTEX and MTBE concentrations near the source area from 1993 to 1997. This suggests that source removal and natural attenuation have been effective in decreasing contaminant concentrations in that area. Continuous increase in MTBE concentration at a well located about 120m downgradient from the source (to a high of 41,400 μg/L in January 1997) indicates that MTBE still is migrating downgradient. Comparison with BTEX

concentrations at the well indicates that BTEX is retarded with respect to MTBE. The presence of TBA in the plume at this time cannot be used to infer degradation of MTBE because of the possibility that TBA existed in the original gasoline. Aerobic conditions exist outside and along the periphery of the plume, and anaerobic conditions, with evidence of a range of redox conditions, are present within the plume, where BTEX and MTBE concentrations are highest. Analysis of gas-phase concentrations of BTEX and MTBE in the unsaturated zone indicates a mass flux of MTBE from the water table on the same order of magnitude as BTEX. Gas concentrations of both BTEX and MTBE within the unsaturated zone decline more sharply that predicted assuming transport with no transformation. To date, analysis of groundwater from five other sites of both point source and nonpoint-source release of MTBE have not detected TBA or TBF.

Carpenter, P.L., and Vinch, C.A.

Carpenter, P.L., and Vinch, C.A., 1997. Remediation of overlapping benzene/MTBE and MTBE-only plumes--A case study, *in* Stanley, Anne, ed.: NWWA/API Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation Conference, Houston, Tex., Nov. 12-14, 1997, [Proceedings]: Houston, Tex., National Water Well Association and American Petroleum Institute, pp. 74-88.

Two overlapping dissolved hydrocarbon plumes were identified in the shallow water bearing zone at a commercial vehicle service and fueling facility. Plume 1 originated from a pre-1993 gasoline product line/dispenser leak. This plume contained a relatively common mix of benzene, toluene, ethylbenzene, xylenes MTBE; benzene and MTBE were identified as the Plume 1 contaminants of concern based on their detection at approximately 200 μg/L each, which exceeded regulatory guidance. Plume 2, which was detected in the tank cavity during UST removal, resulted from gasoline line leaks/underground storage tank overfills. Although the majority of impacted soils in both the dispenser and tank cavity areas were removed during the UST excavation, rainfall during impacted soil removal mobilized the MTBE contained in the soils to the groundwater. As a result, Plume 2 contained approximately 900 μg/L MTBE while BTEX compounds were non-detect. Although the impacted zone sustained an approximate yield of only 0.3-gallon per minute, Pennsylvania regulations dictate that this zone must be treated as an aquifer.

Pump-and-treat was selected as a viable remedial option for the MTBE portions of the plumes. However, managing the impacted water in a cost-effective manner once it reached the surface was a challenge because MTBE does not volatilize easily by sparging/stripping, it does not adhere well to granular activated carbon, and ex-situ biocell treatment with engineered bacteria was still in the development stage. In addition, although pump-and-treat appeared to be the most viable solution for the MTBE portions of the plume, the prospect of reducing benzene concentrations to within regulatory limits using pump-and-treat alone was not attractive, given its historically poor track

record as a remedial option. Therefore, oxygen-releasing-compound (ORC™) slurry was introduced to the water-bearing zone to increase the dissolved oxygen levels in groundwater, thereby enhancing the natural aerobic biodegradation already noted at the site. Thus, MTBE-impacted water was discharged to the local POTW with in-situ rather than ex-situ pre-treatment for benzene.

Dissolved oxygen levels in the wells located downgradient of the ORC™ slurry injection increased; benzene concentrations in Plume 1 decreased to levels acceptable for POTW discharge. The accelerated groundwater flow induced by pumping moved the oxygen-enriched groundwater through the impacted area more quickly than by natural gradient alone. The reduction of dissolved oxygen to concentrations below background suggests increased microbial activity. Fluctuations in BTEX, MTBE, and naphthalene concentrations in Plume 1 appear to be related, at least in part, to the heterogeneity of the aquifer materials. The preferential flow paths exaggerated by the inconsistent aquifer materials affect contaminant transport/availability, nutrient/oxygen availability, and microbial movement within the water-bearing zone.

Church, C.D., L.M. Isabelle, J.F. Pankow, P.G. Tratnyek, D.L. Rose

Church, C.D., L.M. Isabelle, J.F. Pankow, P.G. Tratnyek, D.L. Rose, 1997. Assessing the in situ degradation of methyl *tert*-butyl ether (MTBE) by product identification at the sub-ppb level using direct aqueous injection GC/MS, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 411-413.

The goal of this study is to characterize the kinetics and mechanisms of in situ MTBE degradation, in order to provide a better basis for assessment of its impact and potential for remediation. To do this, it is necessary to establish the major pathways of MTBE degradation, and have methods capable of monitoring the expected products.

Determination of most MTBE degradation products by EPA Standard Method 602,624 is impractical due to their low Henry's Gas Law constants. Direct aqueous injection (DIA) is one way to obtain the full range of likely MTBE degradation products. In order to obtain low detection limits for MTBE and the full suite of its potential degradation products, a DAI method that uses splitless injection and a highly polar column has been developed. Splitless injection ensures maximum sensitivity by delivering 100% of the injected analyte to the column.

Church, C.D., L.M. Isabelle, J.F. Pankow, D.L Rose, P.G. Tratnyek

Church, C.D., L.M. Isabelle, J.F. Pankow, D.L Rose, P.G. Tratnyek, 1997. Method for determination of methyl-*tert*-butyl ether (MTBE) and its degradation products in water: Environmental Science & Technology, v. 31, no. 12, pp. 3723-3726.

An analytical method is described that can detect the major alkyl ether compounds that are used as gasoline oxygenates (MTBE, ETBE, and TAME) and their most characteristic degradation products (TBA, TBF, TAA) in sub-ppb concentrations. The new method involves gas chromatography (GC) with direct aqueous injection (DAI) onto a polar column via a splitless injector, coupled with detection by mass spectrometry (MS). DAI-GC/MS gives excellent agreement with conventional purge-and-trap methods for MTBE over a wide range of environmentally relevant concentrations. The new method can also give simultaneous identification of polar compounds that might occur as degradation products of gasoline oxygenates, such as TBA, TBF, TAA, methyl acetate, and acetone. When the method was applied to effluent from a column microcosm prepared with core material from an urban site in New Jersey, conversion of MTBE to TBA was observed after a lag period of 35 days. However, to date, analyses of water samples from six field sites using the DAI-GC/MS method have not produced evidence for the expected products of in situ degradation of MTBE.

Cline, P.V., J.J. Delfino, P.S.C. Rao

Cline, P.V., J.J. Delfino, P.S.C. Rao, 1991. Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures: Environmental Science & Technology, v. 25, no. 5, pp. 914-920.

Variations in gasoline composition (source variations) as well as complexity in composition (non-ideal behavior, cosolvent effects) contributing to variability in gasoline-water partitioning of aromatic hydrocarbon constituents were examined. Aromatic hydrocarbon concentrations in water extracts of 31 gasoline samples varied over 1 order of magnitude, reflecting the diversity in gasoline composition. However, the gasoline-water partition coefficients (K_{fw}) varied by less than 30% among these samples. Partitioning between water and known mixtures of aromatic and aliphatic solvents was measured and used to estimate the upper and lower bounds of K_{fw} values for more complex solvent mixtures such as gasoline and diesel fuel. Oxygenated additives, such as methanol and methyl tert-butyl ether (MTBE), were shown to have minimal cosolvent effects on hydrocarbon partitioning. The observed inverse, log-log linear dependence of K_{fw} values on aqueous solubility could be well predicted by assuming gasoline to be and ideal solvent mixture (i.e., Raoult's law is valid).

Converse, B.M., and Schroeder, E.D.

Converse, B.M., and Schroeder, E.D., 1998. Estimated Cost Associated with Biodegradation of MTBE, Vol. V: Risk Assessment, Exposure Assessment, Water Treatment & Cost-Benefit Analysis, Report to the Governor and Legislature of the State of California as Sponsored by SB 521, Hydrologic Science, Department of Land, Air and Water Resources, University of California, Davis, Nov. 12, 7 p.

The purpose of this study was to estimate the cost of biological treatment of water and air contaminated with MTBE

Cowan, R.M., and Park, K.

Cowan, R.M., and Park, K., 1996. Biodegradation of the Gasoline Oxygenates MTBE, ETBE, TAME, TBA, and TAA by Aerobic Mixed Cultures, *in* Proceedings of the 28th Mid-Atlantic Conference, July 15-17, 1996: Buffalo NY, pp. 523-530.

Describes the development of aerobic enrichment cultures that mineralize MTBE, ETBE, TAME, TBA, and TAA as their sole source of carbon and energy and presents kinetic and stoichiometric parameter estimates that quantitatively define the degradative ability of these cultures.

Daniel, R.A.

Daniel, R.A., 1995. Intrinsic bioremediation of BTEX and MTBE--Field, laboratory and computer modeling studies: Raleigh, North Carolina State University, Master's thesis, 325 p.

Intrinsic bioremediation was studied at a gasoline contaminated aquifer in Sampson County, NC. A plume of dissolved hydrocarbons has traveled over 600 feet from the source and contains the gasoline oxygenate methyl tert-butyl ether (MTBE). Monitoring wells are located along four cross-sections of the plume and have been used to define the horizontal and vertical distribution of contaminates. Intrinsic bioremediation of the aquifer is proceeding under mixed aerobic and denitrifying conditions with background levels of oxygen above 6 mg/L and nitrate levels typically above 10 mg/L as N. Sampling results over the past year and a half indicate that the plume is not growing and has reached a pseudo-steady-state. Field rates of intrinsic decay were determined by estimating the mass flux of contaminants across each plume cross-section. The results of this method suggest that MTBE degradation occurs near the source area at a rate of 0.18%/day, but is not degrading at other locations in the plume. The ability of indigenous microorganisms to biodegrade MTBE and BTEX was evaluated with laboratory microcosm studies using soil from three locations along the plume centerline.

Aerobic microcosms constructed with source-area soil showed degradation of MTBE during weeks 2 through 7. Loss of MTBE was accompanied by the production of small amounts of tert-butyl alcohol (TBA), a possible transformation intermediate. Degradation stopped after MTBE concentrations decreased from 2 mg/L to approximately 1 mg/L.

The contaminant transport and biodegradation model, BIOPLUME II, and a three dimensional analytical solution were also used to evaluate intrinsic bioremediation of MTBE and BTEX at the site. The modeling results indicate MTBE degradation only occurs near the source. The decay rate

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of all BTEX compounds appears most rapid near the source and decreases further downgradient from the source.

Davidson, J.M.,

Davidson, J.M., 1995. Fate and transport of MTBE--The latest data, *in* Stanley, Anita, ed.: NWWA/API Petroleum Hydrocarbons & Organic Chemicals in Ground Water--Prevention, Detection, and Remediation Conference, Houston, Tex., 1995, [Proceedings]: Houston, Tex., National Water Well Association and American Petroleum Institute, pp. 285-301.

Contrary to early studies, recent research has shown that dissolved-phase methyl-tertiary-butyl ether (MTBE) does not cause significant co-solvency of aromatic hydrocarbons in groundwater. Recent fate and transport studies have also shown that MTBE does not inhibit the natural, beneficial, aerobic biodegradation of benzene, toluene, ethylbenzene, xylenes (BTEX) or other aromatic hydrocarbons. No process exists by which MTBE concentrations can "build-up" or accumulate in the groundwater to concentrations greater that the incoming source. MTBE plumes from blended gasoline spills are typically 1.5 to 2.0 times larger than the associated BTEX plumes due to the natural attenuation of BTEX. Combining national water use statistics with MTBE analyses from drinking water supplies indicates that less than 0.011% of the national population may have more than 200 μg/L of MTBE in their drinking water supply.

Also summarized are the results from the 1995 USGS national groundwater assessment program.

Davidson, J.M., and Parsons, R.

Davidson, J.M., and Parsons, R., 1996. Remediating MTBE with current and emerging technologies, *in* Stanley, Anita, ed.: NWWA/API Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Remediation Conference, Houston, Tex., Nov. 13-15, 1996, [Proceedings]: Houston, Tex., National Water Well Association and American Petroleum Institute, pp. 15-29.

Three major areas are covered in this paper. Factors impacting MTBE remediation such as the compound characteristics, contaminant transport and vertical and horizontal distribution and remediation goals are discussed. Current technologies for MTBE are discussed and performance data from several case studies are interpreted. The third area of discussion is costs of remediating MTBE plumes compared to costs of BTEX plumes without MTBE.

Drobat, P.A., C.A. Bleckrnann, A. Agrawal

Drobat, P.A., C.A. Bleckrnann, A. Agrawal, 1997. Determination of the cometabolic biodegradation potential of methyl tertiary butyl ether in laboratory microcosms, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 405-406.

This is a proposed investigation aimed at expanding the current knowledge by examining the cometabolic biodegradation potential of MTBE with aquifer samples collected from a site (Flint Michigan) with a 7-year history of repeated MTBE contamination. This study is unique, as no current studies cited in the literature appear to have utilized aquifer soil samples from known MTBE contaminated sites, only those where BTEX were the contaminants of concern. The purpose of this study is several fold:

- Demonstrate that MTBE can be cometabolically biodegraded;

- Determine the optimal degradation conditions and limiting factors for such transformation; and

- Characterize the microbes responsible for this biodegradation.

The experiments are being conducted using sediment collected from a MTBE-gasoline contaminated site indicated above. Both batch and column experiments will be performed in aerobic and anaerobic conditions. Chemical analyses are performed using gas and liquid chromatography. A respirometer is utilized in aerobic experiments to measure carbon dioxide demand and oxygen production by microorganisms frequently through the biodegradation process.

Eweis, J.B., E.D. Schroeder, D.P.Y. Chang, K.M., Scow

Eweis, J.B., E.D. Schroeder, D.P.Y. Chang, K.M., Scow, 1998. Biodegradation of MTBE in a Pilot-Scale Biofilter, The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998, [Proceedings]: Columbus, Ohio, Battelle Press, v. C1-3, pp. 341-346.

A pilot-scale biofilter was inoculated with an MTBE degrading culture. The biofilter acclimated within three weeks, and achieved greater than 95% removal of MTBE (based on inlet MTBE concentrations averaging 35 ppmv), at the end of 10 weeks. The biofilter was fed the same concentration of MTBE for about 180 days, and achieved close to 100% removal consistently. Toluene was then introduced at a concentration of about 8 ppmv initially, then 25 and 70 ppmv, over a period of 3 weeks, while the MTBE concentration was maintained the same. The biofilter acclimated quickly to toluene, achieving greater than 90% removal within the first 6 hours. The

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presence of toluene at 8 and 25 ppmv did not seem to influence MTBE degradation. At 70 ppmv toluene however, both MTBE and toluene removal efficiency dropped gradually to less than 70 % over the period of 8 days. This drop was believed to be the result of nitrogen limitation in the biofilter. The same drop in removal efficiency was observed when the biofilter was fed a higher concentration of MTBE (70 ppmv), after toluene feed has been cut off. An increase in the nitrogen concentration in the nutrient solution feed, resulted in almost complete recovery of the biofilter.

Eweis, J.B., N. Watanabe, E.D. Schroeder, D.P.Y. Chang, K.M. Scow

Eweis, J.B., N. Watanabe, E.D. Schroeder, D.P.Y. Chang, K.M. Scow, 1998. MTBE biodegradation in the presence of other gasoline components, *in* The Southwest Focused Ground Water Conference--Discussing the Issue of MTBE and Perchlorate in Ground Water, Anaheim, Calif., June 3-4, 1998, [Proceedings]: Anaheim, Calif., National Ground Water Association, pp. 55-62.

A microbial culture degrading MTBE was tested for its ability to degrade additional fuel oxygenates and gasoline components. The fuel oxygenates considered were TAME, DIPE, and ETBE, and the gasoline components included benzene, toluene, n-hexane and methylcyclopentane. The experiments were conducted in batch liquid culture with MTBE being introduced in combination with each other of the other contaminants. Another objective of the experiments was to investigate the effect of the presence of the additional contaminate on MTBE biodegradation. Results showed that the microbial culture was able to degrade TAME, benzene and toluene with little or no effect on MTBE biodegradation. The culture was not able to degrade the other contaminants however, and the presence of those contaminants had no effect on MTBE degradation. A separate experiment was then conducted to investigate the ability of the culture to biodegrade MTBE. Samples of the MTBE-degrading culture were fed toluene only, for different amounts of time (up to 4 weeks), and then switched back to MTBE only. The cultures were able to degrade MTBE once it was introduced again with little or no lag.

Fogg, G.E., M.E. Meays, J.C. Trask, C.T. Green, E.M. LaBolle, T.W. Shenk, D.E. Rolston

Fogg, G.E., M.E. Meays, J.C. Trask, C.T. Green, E.M. LaBolle, T.W. Shenk, D.E. Rolston, 1998. Impacts of MTBE on California Groundwater, Vol. IV: Groundwater and Surface Water, Health and Environmental Assessment of MTBE, Report to the Governor and Legislature of the State of California as Sponsored by SB 521, Hydrologic Science, Department of Land, Air and Water Resources, University of California, Davis, Nov. 12, 101 p.

Addresses 1) current impacts of MTBE to the state's groundwater used for drinking; 2) risks to the state's groundwater resources associated with MTBE leaking from storage tanks and other

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presence of toluene at 8 and 25 ppmv did not seem to influence MTBE degradation. At 70 ppmv toluene however, both MTBE and toluene removal efficiency dropped gradually to less than 70 % over the period of 8 days. This drop was believed to be the result of nitrogen limitation in the biofilter. The same drop in removal efficiency was observed when the biofilter was fed a higher concentration of MTBE (70 ppmv), after toluene feed has been cut off. An increase in the nitrogen concentration in the nutrient solution feed, resulted in almost complete recovery of the biofilter.

Eweis, J.B., N. Watanabe, E.D. Schroeder, D.P.Y. Chang, K.M. Scow

Eweis, J.B., N. Watanabe, E.D. Schroeder, D.P.Y. Chang, K.M. Scow, 1998. MTBE biodegradation in the presence of other gasoline components, *in* The Southwest Focused Ground Water Conference--Discussing the Issue of MTBE and Perchlorate in Ground Water, Anaheim, Calif., June 3-4, 1998, [Proceedings]: Anaheim, Calif., National Ground Water Association, pp. 55-62.

A microbial culture degrading MTBE was tested for its ability to degrade additional fuel oxygenates and gasoline components. The fuel oxygenates considered were TAME, DIPE, and ETBE, and the gasoline components included benzene, toluene, n-hexane and methylcyclopentane. The experiments were conducted in batch liquid culture with MTBE being introduced in combination with each other of the other contaminants. Another objective of the experiments was to investigate the effect of the presence of the additional contaminate on MTBE biodegradation. Results showed that the microbial culture was able to degrade TAME, benzene and toluene with little or no effect on MTBE biodegradation. The culture was not able to degrade the other contaminants however, and the presence of those contaminants had no effect on MTBE degradation. A separate experiment was then conducted to investigate the ability of the culture to biodegrade MTBE. Samples of the MTBE-degrading culture were fed toluene only, for different amounts of time (up to 4 weeks), and then switched back to MTBE only. The cultures were able to degrade MTBE once it was introduced again with little or no lag.

Fogg, G.E., M.E. Meays, J.C. Trask, C.T. Green, E.M. LaBolle, T.W. Shenk, D.E. Rolston

Fogg, G.E., M.E. Meays, J.C. Trask, C.T. Green, E.M. LaBolle, T.W. Shenk, D.E. Rolston, 1998. Impacts of MTBE on California Groundwater, Vol. IV: Groundwater and Surface Water, Health and Environmental Assessment of MTBE, Report to the Governor and Legislature of the State of California as Sponsored by SB 521, Hydrologic Science, Department of Land, Air and Water Resources, University of California, Davis, Nov. 12, 101 p.

Addresses 1) current impacts of MTBE to the state's groundwater used for drinking; 2) risks to the state's groundwater resources associated with MTBE leaking from storage tanks and other

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petroleum storage and conveyance facilities; and 3) potential future risks to the state's groundwater should MTBE continue to be used

Garrett, P., M. Moreau, J.D. Lowry

Garrett, P., M. Moreau, J.D. Lowry, 1986. MTBE as a ground water contaminant, *in* NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Restoration, Houston, Tex., November 12-14, 1986, [Proceedings]: Dublin, Ohio, National Water Well Association, pp. 227-238.

Several sites were investigated in which groundwater contamination occurred by spills of gasoline with MTBE. In one case, several household wells became contaminated with MTBE only. In one household, concentrations of up to 690 ppb MTBE were measured, (with other gasoline constituents combined at less than 10 ppb). The well nearest the spill had concentrations of up to 126,000 ppb gasoline including MTBE. At another site, concentrations exceeded 600,000-ppb gasoline including MTBE. This contrasts with the usual maximum dissolved concentration of gasoline in groundwater near spill sites of about 10-30,000 ppb (when no MTBE is present).

Grady, S.J.

Grady, S.J., 1997. Distribution of MTBE in ground water in New England by aquifer type and land use, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 392-394.

MTBE was the most frequently detected of 25 VOCs found in groundwater samples collected from 1993 to 1995 at wells in the Connecticut, Housatonic, and Thames River Basins. MTBE was detected at concentrations as great as 5.8 mg/L in 25 percent of monitoring wells screened in surficial aquifers and in 23 percent of domestic and institutional water-supply wells in fractured bedrock aquifers. The presence of MTBE in groundwater is related to urban land use, and the frequency of MTBE detections increased with population density. No significant difference in MTBE detections was observed when the depths of wells were compared for surficial and bedrock aquifers independently. The low concentrations if MTBE observed and the general lack of concurrent BTEX detections indicate that the MTBE in groundwater is from non-point sources, such as atmospheric deposition and recharge from urban runoff.

Hanson, J., K. Scow, M.A. Bruns, T. Brethour

Hanson, J., K. Scow, M.A. Bruns, T. Brethour, 1998. Characterization of MTBE-Degrading Bacterial Isolates and associated Consortia, [abs] Land Air & Water Resources, University of California, Davis, June. http://www.tsrtp.ucdavis.edu/tsrtp/MTBE_RFP/june_abstracts/scow_hanson.html, 1p.

Contrary to some previous reports, methyl tertiary butyl ether (MTBE) can be biodegraded. We have isolated two bacterial strains, PM1 and YM1, which can use MTBE as their only source of carbon and energy. These strains were obtained from mixed microbial consortium provided by the University of California, Davis Department of Civil and Environmental Engineering. MTBE degradation by PM1 is rapid (complete disappearance of the pollutant within 4 days), and is not affected by the addition of small amounts of nutrients., YM1 degrades MTBE more slowly (50% degraded in 4 days) and nutrients appear to enhance MTBE degradation. Examination of whole cell lipid profiles for PM1 and YM1 indicates that they are not identical strains. Thermal gradient gel electrophoresis (TGGE) analysis of 16S rRNA gene fragments from the two strains, however, showed no difference between them. 16S rDNA sequence analysis of strains PM1 and YM1 revealed that they are both most closely related to the genus *Sphingomonas*.

In addition to describing of the MTBE-degrading isolates, we have begun to examine their importance in the MTBE-degrading mixed culture. Fingerprinting methods that analyze cell components (e.g. phospholipids, DNA) extracted directly from mixed cultures and environmental samples can provide insight into the composition and stability of microbial communities. Analysis of DNA by TGGE indicated that neither of the bacterial isolates described above made up dominant bands in the MTBE-grown microbial consortium. An additional unidentified band was particularly dominant when the consortium was cultured on MTBE. We are currently working to obtain the DNA sequence of this band.

Happel, A.M., E.H. Beckenbach, R.U. Halden

Happel, A.M., E.H. Beckenbach, R.U. Halden, 1998. An evaluation of MTBE impacts to California groundwater resources: Livermore, Calif., Lawrence Livermore National Laboratory, UCRL-AR-130897, June, 11, 68 p.

1. <u>MTBE is a frequent and widespread contaminant in shallow groundwater throughout California</u>. There are presently 32,409 LUFT sites recognized in the state, 13,278 at which hydrocarbons are known to have impacted groundwater. A minimum estimate of the number of MTBE-impacted sites in California is greater than 10,000.

2. <u>MTBE plumes are more mobile than BTEX plumes</u>. Although our results using 1995/96 data indicate that, at the majority of sites, individual MTBE plumes were nearly equivalent or shorter than their corresponding benzene plumes (defined by action levels of 20 and 1 μg L^{-1} respectively), our results predict that at a portion of these sites this relationship will change over time as the contaminant plumes gradually dissociate.

3. <u>The primary attenuation mechanism for MTBE is dispersion</u>. Observed attenuation of BTEX and MTBE compounds at downgradient monitor wells suggests that MTBE is

not significantly degrading in existing monitoring networks. Thus, MTBE may be regarded as recalcitrant under site-specific conditions. MTBE concentrations leaving these networks were greater than those of BTEX compounds at a significant portion of LUFT sites. Assuming resistance of MTBE to biodegradation, these plumes will eventually attenuate to regulatory concentration goals due to dispersion, although in contrast to BTEX compounds, the mass would not be depleted and significantly longer distances and time frames would be required.

4. <u>MTBE has the potential to impact regional groundwater resources and may present a cumulative contamination hazard</u>. To date, impacts of MTBE to public water systems have been limited and were similar in frequency to those of benzene. Based on historical data, future impacts of aromatic hydrocarbons, such as benzene, to water supplies is not expected to be common, due to retardation and relative ease of biodegradation. In contrast, MTBE contamination may be a progressive problem due to the chemical's apparent recalcitrance and mobility. With a compound that appears both ubiquitous and recalcitrant, water resource management on the regional scale will become increasingly relevant. For example, the potential long-term accumulation of mass resulting from dispersion of MTBE plumes may be a key consideration for management of specific regional groundwater basins. Therefore, leak prevention is a critical requirement for the continued use of MTBE to ensure future protection of drinking water resources.

5. We have identified two major areas of uncertainty in our results. First, presently available MTBE data are limited. Second, the issue of recalcitrance of MTBE has not been resolved. Ideally, time-series data from hundreds of LUFT sites representing all hydrogeologic regions of California should be utilized to characterize the behavior and impact of MTBE plumes. Analyses of an expanded dataset are important to confirm our initial findings regarding the mobility and recalcitrance of MTBE at California LUFT sites. Further time-series analyses are necessary for predicting future MTBE impacts to groundwater resources, and assessing the vulnerability of drinking water resources.

A number of laboratory-cultured microorganisms isolated from various environments can degrade MTBE, yet there is no convincing evidence to date that this destructive process occurs quickly and/or commonly in the field. While future research is warranted to address these issues, it is appropriate to manage groundwater resources with the assumption that MTBE is both mobile and recalcitrant relative to benzene, until proven otherwise.

Hardison, L.K., S.S. Curry, L.M. Ciuffetti, M.R. Hyman

Hardison, L.K., S.S. Curry, L.M. Ciuffetti, M.R. Hyman, 1997. Metabolism of Diethyl Ether and Cometabolism of Methyl tert-Butyl Ether by a Filamentous Fungus, a *Graphium* sp.: Applied and Environmental Microbiology, v., 63, no. 8, pp. 3059-3067.

In this study, evidence for two novel metabolic processes catalyzed by a filamentous fungus, *Graphium* sp. strain ATCC 58400, is presented. First, our results indicate that this *Graphium* sp. can utilize the widely used solvent diethyl ether (DEE) as the sole source of carbon and energy for growth. The kinetics of biomass accumulation and DEE consumption closely followed each other, and the molar growth yield on DEE was indistinguishable from that with n-butane. n-Butane-grown mycelia also immediately oxidized DEE without the extracellular accumulation of organic oxidation products. This suggests a common pathway for the oxidation of both compounds. Acetylene, ethylene, and other unsaturated gaseous hydrocarbons completely inhibited the growth of this Graphium sp. on DEE and DEE oxidation by n-butane-grown mycelia. Second, our results indicate that gaseous n-alkane-grown Graphium mycelia can cometabolically degrade the gasoline oxygenate MTBE. The degradation of MTBE was also completely inhibited by acetylene, ethylene, and other unsaturated hydrocarbons and was strongly influenced by n-butane. Two products of MTBE degradation, TBF and TBA were detected. The kinetics of product formation suggest that TBF production temporally precedes TBA accumulation and that TBF is hydrolyzed both biotically and abiotically to yield TBA. Extracellular accumulation of TBA accounted for only a maximum of 25% of the total MTBE consumed. Our results suggest that both DEE oxidation and MTBE oxidation are initiated by cytochrome P-450-catalyzed reactions that lead to scission of the ether bonds in these compounds. Our findings also suggest a potential role for gaseous n-alkane-oxidizing fungi in the remediation of MTBE contamination.

Hickman, G.T., and Novak, J.T.

Hickman, G.T., and Novak, J.T., 1989. Relationship between subsurface biodegradation rates and microbial density: Environ. Sci. Technol., v. 23, no. 5, pp. 525-532.

Rates and patterns of biodegradation of methanol, phenol and TBA in surface and subsurface soils were evaluated in static microcosms. Biodegradation rates in subsurface soils generally were within the ranges 0.5-1.1 mg/L/d for methanol, 0.4-1.1 mg/L/d for phenol, and 0.1-0.3 mg/L/d for TBA (linear approximations normalized by soil dry weight; initial concentration, 100 mg/L; incubation temperature, 20 degrees Celsius). Microbial density was measured in soils by plate counting (aerobic and anaerobic), by substrate-specific MPN analysis, and by direct microscopical counting. Linear regression was employed to determine if biodegradation rates were correlated to microbial measures of the soils. The two types of data were directly related, but correlation coefficients were generally low. Coefficients of determination indicated that, at best, 87%, 92%,

and 37% of the variability in subsurface biodegradation rates of methanol, phenol, and TBA, respectively, could be attributed to differences in the measures of bacterial density.

Horan, C.M., and Brown, E.J.

Horan, C.M., and Brown, E.J., 1995. Biodegradation and inhibitory effects of methyl-tertiary-butyl ether (MTBE) added to microbial consortia, *in* Annual Conference on Hazardous Waste Research, 10th, Manhattan, Kansas State University, May 23-24, 1995, [Proceedings]: pp. 11-19.

It was found that MTBE added to carbon-limited microbial consortia increased oxygen consumption but that concentrations approaching 740 mg/L inhibited the mineralization potential of another fuel constituent (hexadecane) by up to 50%. These results indicate that MTBE can be metabolized in the environment but that toxicity may adversely affect the overall biodegradation of hydrocarbon constituents of liquid fuels.

Hubbard, C.E., J.F. Barker, M. Vandegriendt

Hubbard, C.E., J.F. Barker, M. Vandegriendt, 1994. Transport and fate of dissolved methanol, methyl-tertiary-butyl-ether, and monoaromatic hydrocarbons in a shallow sand aquifer--Appendix H--Laboratory biotransformation studies: Washington, D.C., Health and Environmental Sciences Department, American Petroleum Institute Publication No. 4601, 75 p.

Hubbard, C.E., J.F. Barker, S.F. O'Hannesin, M. Vandegriendt, R.W. Gillham

Hubbard, C.E., J.F. Barker, S.F. O'Hannesin, M. Vandegriendt, R.W. Gillham, 1994. Transport and fate of dissolved methanol, methyl-tertiary-butyl-ether, and monoaromatic hydrocarbons in a shallow sand aquifer: Washington, D.C., Health and Environmental Sciences Department, American Petroleum Institute Publication No. 4601, 102 p.

Presents the results of a field investigation of the fate and transport of two gasoline additives, methanol and MTBE, in groundwater and the influence of these compounds on the groundwater fate and transport of the gasoline constituents benzene, toluene, ethylbenzene, and xylene (BTEX). Related laboratory experiments which are the subject of a separate report are also summarized.

Hyman, M., P. Kwon, K. Williamson, K. O'Reilly

Hyman, M., P. Kwon, K. Williamson, K. O'Reilly, 1998. Cometabolism of MTBE by Alkane – Utilizing Microorganisms, The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998, [Proceedings]: Columbus, Ohio, Battelle Press, pp. 321-326.

We have established that a wide variety of microorganisms cometabolically degrade methyl tert-butyl ether (MTBE) after growth on alkanes. Here we describe the initial products and kinetics of MTBE oxidation by an alkane-grown *Xanthobacter* strain and we compare these results with similar studies conducted with other alkane-utilizing microorganisms. Like the propane-oxidizing fungus (*Graphium*) and the bacterium (*Mycobacterium vaccae*), the immediate product of MTBE oxidation by propane-grown *Xanthobacter* is tert-butyl formate, which subsequently hydrolyzes to tert-butyl alcohol (TBA). The K_m for MTBE for propane-grown *Xanthobacter* is 2.4 mM (210 ppm). Acetylene (C_2H_2) inactivates propane-, MTBE- and TBA-oxidizing activity in *Xanthobacter* and M. *vaccae* but has no effect on 1-propanol oxidation by either organism. This suggests MTBE and TBA are both oxidized by the oxygenase enzyme responsible for initiating propane oxidation. In contrast, ethylene (C_2H_4) does not inactivate MTBE-oxidizing activity and this suggest that alkane and MTBE oxidation is not catalyzed by a cytochrome P-450 in these bacteria. The *Xanthobacter* strain, like M. *vaccae*, also oxidizes MTBE after growth on branched alkanes, including the major gasoline component, isopentane. Microcosm studies demonstrate that rapid MTBE degradation can be promoted in soils by isopentane. The bioremediation options for MTBE revealed by this study are discussed.

Javanmardian, M., and Glasser, H.A.

Javanmardian, M., and Glasser, H.A., 1997. In-situ biodegradation of MTBE using biosparging, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, p. 424.

A pilot study was conducted to test in situ biodegradation of MTBE with oxygen being supplied by four low flow biosparging wells. Initial MTBE concentrations in the aquifer ranged from 5-10 ppm. MTBE concentrations in groundwater decreased to non-detect during operation in the oxygenated areas of the plume whereas there was no significant change in non oxygenated (low DO level) areas. Laboratory microcosm studies were conducted to verify that biosparging stimulated indigenous bacteria to biodegrade MTBE in the field. Microcosms containing soil and groundwater samples from aerated portion of the plume showed significant biodegradation of MTBE with a half-life of approximately 30-45 days; whereas the ones from non-aerated portion of the plume exhibited no change in MTBE concentration during the six month analysis period

Jensen, H.M., and Arvin, E.

Jensen, H.M., and Arvin, E., 1990. Solubility and degradability of the gasoline additive MTBE, methyl *tert*-butyl-ether, and gasoline compounds in water, *in* Arendt, F., Hinsenveld, M., and Van Den Brink, W.J., eds.: Contaminated Soil '90: Netherlands, Kluwer Academic Publishers, pp. 445-448.

The water solubility and biodegradation of the gasoline additive MTBE were studied in laboratory batch experiments. The solubility of MTBE in water in equilibrium with a model gasoline mixture with an initial concentration of 6.3 % (w/w) was about 900 mg/l. No biodegradation of 10 mg/l MTBE and 3 mg/l TAME, another gasoline additive was observed after 60 days and 30 days. In contrast, the aromatic hydrocarbons in the model gasoline were all easily degraded within 1-2 weeks or even shorter time. Four types of inoculation material were investigated: a sandy aquifer material, topsoil and two types of activated sludge. A literature search revealed surprisingly little information on these subjects

Karpel Vel Leitner, N., A.L. Papailhou, J.P. Croue, J. Peyrot, M. Dore

Karpel Vel Leitner, N., A.L. Papailhou, J.P. Croue, J. Peyrot, M. Dore, 1994. Oxidation of methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) by ozone and combined ozone/hydrogen peroxide: Ozone Science & Engineering, v. 16, no. 1, pp. 41-54.

The aim of this study was to determine the capability of ozone and combined ozone/hydrogen peroxide treatments to degrade oxygenated additives such as MTBE and ETBE in dilute aqueous solution using controlled experimental conditions. Experiments conducted in a semi-continuous reactor with MTBE and ETBE in combination (initial concentration = 200 mg/L of each) showed that ETBE was better eliminated than MTBE with both ozone and combined O_3/H_2O_2. Batch experiments lead to the determination of the ratio of the kinetic constants for the reaction of OH^o-radical with MTBE and ETBE ($k_{OH}^o{}_{/ETBE}/k_{OH}^o{}_{/MTBE} = 1.7$). Tert-Butyl formate and Tert-Butyl acetate were identified as the ozonation by products of MTBE and ETBE respectively, while Tert-Butyl alcohol was found to be produced during the ozonation of both compounds.

Kharoune, M., L. Bouagache, A. Pauss, J.M. Lebeault

Kharoune, M., L. Bouagache, A. Pauss, J.M. Lebeault, Biological and Photochemical Treatment of the Unleaded Gasoline Oxygenates: MTBE, ETBE and TAME, Division des Procédés Biotechnologiques, Université de Technologie de Compiègne, F., pp. 381-384.

Ethyl Tert Butyl Ether (ETBE)-mineralizing microorganisms were isolated from polluted soil. N batch cultures, the acclimated cells used ETBE as sole source of carbon and energy. The ETBE removal rates, when it was treated alone or in mixture with Tert Amyl Methyl Ether (TAME) an MTBE, were about 4 mg/L/D and 2 mg/L/d respectively.

In the second part of this study, the photolytic pretreatment of ETBE was investigated in batch annular reactor equipped with a low-pressure mercury lamp. Depending on the initial hydrogen peroxide concentration, transformation higher than 99% of 10 mmol/L of ETBE can be achieved in less than 30 minutes of irradiation using 50 mmol/L of H_2O_2. The by-products formed in these

conditions can be biodegraded by the acclimated strains as well as by the unacclimated municipal sludge.

The results of this study suggest that combined H_2O_2/UV and biological processes can be applicable to the overall treatment of wastewater containing such recalcitrant compounds as ETBE.

Landmeyer, J.E., F.H. Chapelle, P.M. Bradley

Landmeyer, J.E., F.H. Chapelle, P.M. Bradley, 1996. Assessment of intrinsic bioremediation of gasoline contamination in the shallow aquifer, Laurel Bay Exchange, Marine Corps Air Station, Beaufort, South Carolina: U.S. Geological Survey Water-Resources Investigations Report 96-4026, 50 p.

Laboratory, field, and digital solute-transport-modeling studies demonstrate that microorganisms indigenous to the shallow ground-water system at Laurel Bay Exchange, Marine Corps Air Station Beaufort, South Carolina, can degrade petroleum hydrocarbons in gasoline released at the site. MTBE concentrations are also presented for the site, although this report does not assess the intrinsic bioremediation of MTBE.

Landmeyer, J.E., J.F. Pankow, C.D. Church

Landmeyer, J.E., J.F. Pankow, C.D. Church, 1997. Occurrence of MTBE and *tert*-butyl alcohol in a gasoline-contaminated aquifer, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 413-415.

A leaking UST at the Laurel Bay Exchange, Marine Corps Air Station, Beaufort, South Carolina released unknown amount of gasoline in September 1991. This abstract documents the first field observation of the co-occurrence of both MTBE and its degradation intermediate tert-butyl alcohol (TBA). However, the presence of TBA at the site is not conclusive evidence of MTBE transformation, because TBA has been used in the past as an octane enhance and could have been a part of the fuel spilled. [TBA]/[MTBE] ratios are employed in elucidating a potential source of TBA.

Landmeyer, J.E., F.H. Chapelle, P.M. Bradley, J.F. Pankow, C.D. Church, P.G. Tratnyek

Landmeyer, J.E., F.H. Chapelle, P.M. Bradley, J.F. Pankow, C.D. Church, P.G. Tratnyek, 1998. Fate of MTBE relative to benzene in a gasoline-contaminated aquifer (1993-98): Ground Water Monitoring & Remediation, Fall, pp. 1-10.

MTBE and benzene have been measured since 1993 in a shallow, sandy aquifer contaminated by a mid-1980's release of gasoline containing fuel oxygenates. In wells downgradient of the

release area, and also up to 10 feet (3 meters) below the water-table surface in nested wells located farther from the release area. This distribution of higher concentrations at depth is caused by recharge events that deflect originally horizontal ground-water flowlines. In the laboratory, microcosms containing aquifer material incubated with uniformly labeled ^{14}C-MTBE under aerobic and anaerobic, Fe(III)-reducing conditions indicated a low but measurable biodegradation potential ($<3\%$ ^{14}C-MTBE as $^{14}CO_2$) after a seven-month incubation period. *Tert*-butyl alcohol (TBA), a proposed microbial-MTBE transformation intermediate, was detected in MTBE-contaminated wells, but TBA was also measured in unsaturated release-area sediments. This suggests that TBA may have been present in the original fuel spilled, and not necessarily reflect microbial degradation of MTBE. Combined, these data suggest that milligram per liter to microgram per liter decreases in MTBE concentrations relative to benzene are caused by the natural attenuation processes of dilution and dispersion with less-contaminated ground water in the direction of flow rather than biodegradation at this point-source gasoline release site.

Mace, R.E., and Choi, Wan-Joo

Mace, R.E., and Choi, Wan-Joo, 1998. The Size and Behavior of MTBE Plumes in Texas, *in* Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Prevention, Detection, and Remediation Conference Houston, Texas, Nov. 11-13, 1998, National Ground Water Association, pp. 1-11.

The occurrence of methyl tert-butyl ether (MTBE) in the environment has received considerable scientific attention over the past few years, resulting in substantial reports by the U.S. Geological Survey, the U.S. EPA, and the National Science and Technology Council. Regulators have become more concerned about the behavior of MTBE in the subsurface and its implications for current corrective action procedures. To date, little is known about the size of MTBE plumes in the field or how they compare with benzene plumes, except for a few well-publicized incidents that may be worst-case scenarios. To address this issue, we compiled MTBE and benzene concentration data at 609 leaking petroleum storage tank (LPST) sites and estimated MTBE plume lengths at 99 LPST sites and benzene plume lengths at 289 LPST sites, for a concentration of 10 ppb. Results show that MTBE is detected in shallow ground water beneath 93 percent of LPST sites in most parts of the state. Most sites have maximum MTBE concentrations that exceed the lower limit of the EPA advisory level (85%>20 ppb) and the protective concentration level proposed for Texas (80 % > 40 ppb). Geometric mean plume lengths for MTBE at a concentration of 10 ppb is 182 ft. MTBE plumes extend beyond the edge of the monitoring-well network at about 10 percent of the sites. MTBE plumes are, on average, about 27 feet longer than benzene plumes and are longer that their companion benzene plumes at 56 percent of the sites. Analysis of temporal data (83 percent of wells have stable, decreasing, or non-detection of MTBE concentration; co-occurrence with benzene has remained the same for the past several years; and

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limited plume length data show sites with stable plumes) suggests that MTBE plumes may be naturally attenuated at many sites in Texas. This conclusion of natural attenuation, however, is preliminary. Better site-specific temporal data are needed to confirm the occurrence of natural attenuation of MTBE and to estimate the fraction of sites that have stable, growing or receding plumes.

McCarthy, J.E., and Tiemann, M.

McCarthy, J.E., and Tiemann, M., 1998. CRS Report for Congress, MTBE in gasoline: Clean Air and Drinking Water Issues, Congressional Research Service, 98-290 ENR

Provides background information concerning MTBE and legislation (H.R. 630 / S. 1576) that would address the issue of its use in California reformulated gasoline. Controversy has surrounded the use of MTBE, most recently because of concern over contamination of drinking water supplies by leaking gasoline storage tanks and pipelines. The report briefly summarized information concerning the environmental impacts of the additive's use and potential regulatory and legislative options.

McKinnon, R.J., and Dyksen, J.E.

McKinnon, R.J., and Dyksen, J.E., 1984. Removing organics from groundwater through aeration plus GAC: Journal of the American Water Works Association, v. 76, no. 5, pp. 42-47.

A NJ township installed an aeration system and a granular activated carbon (GAC) system to remove ethers and TCE from groundwater that is used for the public drinking water supply. MTBE was present in the system at concentrations of 25 to 40 μg/L. Removal rates and operation data are presented.

McMahon, P.B., R. Crowfoot, D. Wydoski

McMahon, P.B., R. Crowfoot, D. Wydoski, 1995. Effect of fuel oxidants on the degradation of gasoline components in aquifer sediments [abs.], *in* Poster abstracts, situ and on-site bioreclamation--The third international symposium, April 24-27, 1995, San Diego, Calif.: Battelle, p. D7.

McMahon, P.B., and Bruce, B.W.

McMahon, P.B., and Bruce, B.W., 1997. Distribution of terminal electron-accepting processes in an aquifer having multiple contaminant sources: Applied Geochemistry, v. 12, no. 4, pp. 507-516.

Concentrations of electron acceptors, electron donors, and H_2 in groundwater were measured to determine the distribution of terminal election-accepting processes (TEAPs) in an alluvial aquifer having multiple contaminant sources. Upgradient contaminant sources included two separate hydrocarbon point sources, one of which contained the fuel oxygenate MTBE. Infiltrating river water was a source of dissolved NO_3, SO_4 and organic carbon (DOC) to the downgradient part of the aquifer. Groundwater downgradient from the other hydrocarbon source, suggesting that MTBE was not as suitable for supporting TEAPs as the other hydrocarbons. Measurements of dissolved H_2 indicated that SO_4 reduction predominated in the aquifer during a period of high water levels in the aquifer and river. The predominate TEAP shifted to Fe^{3+} reduction in upgradient areas after water levels receded but remained SO_4 reducing downgradient near the river. This distribution of TEAPs is the opposite of what is commonly observed in aquifers having a single contaminant point source and probably reflects the input of DOC and SO_4 to the aquifer from the river. Results of this study indicate that the distribution of TEAPs in aquifers having multiple contaminant sources depends on the composition and location of the contaminants and on the availability of electron acceptors.

Mihelcic, J.R.

Mihelcic, J.R., 1990. Modeling the potential effect of additives on enhancing the solubility of aromatic solutes contained in gasoline: Ground Water Monitoring & Remediation, v. 10, no. 3, pp. 132-137.

The potential effect of two common gasoline additives, ethanol and MTBE, on enhancing the solubility of the aromatic solutes benzene, toluene, ethylbenzene, and o-, m-, and p-xylene, was examined using a computer model, ARSOL. Aqueous solute systems containing cosolvents ethanol and MTBE at 0, 0.1, 1, and 4.3 percent were modeled for both ethanol and MTBE systems. Five- and 10-percent ethanol systems were also modeled. Little solubility enhancement was predicted by modeling at cosolvent levels less than 1 percent. At cosolvent levels greater than 1 percent, predicted solute solubility increased curvilinearly with an increase in percent cosolvent; a 10 percent cosolvent system increased aromatic hydrocarbon solubility by approximately 100 percent. According to the model predictions, MTBE enhanced solute solubility more than ethanol, with enhancement of MTBE being approximately 10 percent greater that enhancement by ethanol at 4.3 percent cosolvent. Other concerns regarding gasoline additives are the observed reduction in partitioning of solutes to soils and sediments and the contamination of water supplies due to the high water solubility of the additives.

Miller, M.E., D.C. Mosteller, A.W. Bourquin, K.F. Reardon, B.K. Desilets, E.M. Johnson, D. Dumont, M.P. Picard, R.D. Hines Jr., S.T. Kilkenny

Miller, M.E., D.C. Mosteller, A.W. Bourquin, K.F. Reardon, B.K. Desilets, E.M. Johnson, D. Dumont, M.P. Picard, R.D. Hines Jr., S.T. Kilkenny, 1997. Bioreactor Treatment of MTBE and TCE in Contaminated Groundwater, *in* Papers from the Fourth International In Situ and On-Site Bioremediation Symposium: Battelle Press, Columbus, Ohio, v. 5, pp. 89-94.

Groundwater contaminated with various petroleum products and chlorinated aliphatic solvents was treated in two parallel granular activated carbon (GAC) fluidized bed bioreactors (FBBRs). Approximately six weeks following start-up, the carbon active sites appeared to have become saturated and the effluent concentrations better reflected ongoing biodegradation. Total petroleum hydrocarbon (TPH) and benzene, toluene, ethylbenzene, and xylene (BTEX) removal efficiencies were very high at 80% and greater than 99% respectively. Following saturation of the active sites, methyl tertiary-butyl ether (MTBE) removal was very low, until MTBE-degrading cultures were added to the reactor and the percentage removal increased to greater that 75%. Tetrachloroethylene (PCE) and trichlorofluoromethane (TCFM) were removed at approximately 50% of their influent concentrations, indicating possible dechlorination within anaerobic niches of the carbon particles. Trichloroethylene (TCE) and dichloroethylene (DCE) removals at average efficiencies of 47% and 69%, respectively, were believed to be the result of aerobic cometabolism. Carbon samples were plated on colorimetric media, and the results indicated the presence of oxygenase-producing bacteria.

Mo, K., C.O. Lora, A. Wanken, C.F. Kulpa

Mo, K., C.O. Lora, A. Wanken, C.F. Kulpa, 1995. Biodegradation of methyl-*t*-butyl ether by pure bacterial cultures [abs.], *in* Abstracts of the 95th general meeting of the American Society for Microbiology: American Society for Microbiology, v. 95, p. 408.

Three pure bacterial cultures degrading MTBE were isolated from activated sludge and fruit of the Gingko tree. They have been classified as belonging to the genuses *Methlobacterium, Rhodococcus,* and *Arthrobacter.* These cultures degraded 60 ppm MTBE in 1-2 weeks of Incubation at 23-25 $^{\circ}$C. The growth of the isolates on MTBE as sole carbon source is very slow compared with growth on nutrient-rich medium. Uniformly-labeled [^{14}C] MTBE was used to determine $^{14}CO_2$ evolution. Within 7 days of incubation, about 8% of the initial radioactivity was evolved as $^{14}CO_2$. The presence of these compounds in combination with MTBE decreased the degradation of MTBE. The cultures pregrown on pyruvate resulted in a reduction in $^{14}CO_2$ evolution from [^{14}C] MTBE. The availability of pure cultures will allow the determination of the pathway intermediates and the rate-limiting steps in the degradation of MTBE.

Mormile, M.R., S. Liu, J.M. Suflita

Mormile, M.R., S. Liu, J.M. Suflita, 1994. Anaerobic biodegradation of gasoline oxygenates-- Extrapolation of information to multiple sites and redox conditions: Environmental Science & Technology, v. 28, no. 9, pp. 1727-1732.

A series of alcohol, ketone, ester, and ether oxygenates were tested for their susceptibility to decay in samples from four chronically contaminated sedimentary environments. The effect of various electron acceptors on oxygenate biodegradation was also evaluated with a single inoculum source. In addition, two acetogenic bacteria were tested for their ability to metabolize selected oxygenate compounds. The susceptibility of the test oxygenates to anaerobic decay could be related to their chemical structure. That is, compounds other than the ethers that possessed primary or secondary substituted carbon atoms resisted biodegradation.   The other oxygenates were generally not degraded when incubated with various inocula, regardless of the electron acceptor status. The exceptions included methyl butyl ether, which was depleted in both sulfate reducing and methanogenic incubations, and the partial transformation of methyl tert-butyl ether to tert-butanol after a 152-day acclimation period in a single replicate from a river sediment chronically contaminated with fuel.   Heat-inactivated control incubations suggested that the later transformation was biologically catalyzed.   This study provides a basis for assessing the environmental fate characteristics of the frequently used gasoline oxygenates as well as several potential alternate fuel additives.

Novak, J.T., Goldsmith, C.D., Benoit, R.E., and O'Brian, J.H.,

Novak, J.T., C.D. Goldsmith, R.E. Benoit, J.H. O'Brian, 1985. Biodegradation of methanol and tertiary butyl alcohol in subsurface systems: Water Science & Technology, v. 17, pp. 71-85.

The purpose of this study was to determine if and at what rate gasoline based alcohols would be degraded in subsurface system. Soils were obtained from three sites in the USA for microcosm studies. Methanol was found to degrade at all sites up to a concentration of 1000 mg/L such that contamination would be reduced to non-measurable levels in one year or less. Tertiary butyl alcohol (TBA) was more refractory but was biodegraded at all sites. For sites where anaerobic conditions prevailed, degradation rates varied directly with the TBA concentration. The data suggests that methanol contamination problems in groundwater should be minimal because of its susceptibility to biodegradation. TBA may be more persistent but should also degrade.

Odencrantz, J.E.

Odencrantz, J.E., 1998. Implications of MTBE for Intrinsic Remediation of Underground Fuel Tank Sites: Remediation, The Journal of Environmental Cleanup Costs, Technologies & Techniques, Summer 1998, pp. 7-16.

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

Pankow, J.F., N.R. Thompson, R.L. Johnson, A.L. Baehr, J.S. Zogorski

Pankow, J.F., N.R. Thompson, R.L. Johnson, A.L. Baehr, J.S. Zogorski, 1997. The Urban Atmosphere as a Non-Point Source for the Transport of MTBE and Other Organic Compounds (VOCs) to Shallow Groundwater: Environmental Science and Technology, v. 31, no. 10, pp. 2821-2828.

Numerical simulations were conducted using 1-D model domain set in poorly-sorted medium sand (depth to water = 5m) to test whether MTBE and other atmospheric VOCs could move to shallow groundwater within the type of 10 to 15 year time from over which MTBE has been used in large amounts. Degradation and sorption were assumed negligible. Results indicated that MTBE can reach the groundwater from precipitation. Urban air is a potential non-point source for MTBE and other VOCs to reach shallow urban groundwater

Park, K., and Cowan, R.M

Park, K., and Cowan, R.M., 1997. Effects of oxygen and temperature on the biodegradation of MTBE, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 421-424.

Describes the effects of dissolved oxygen and temperature on the biodegradability of MTBE by acclimated cultures. The preliminary study shows that the biodegradation rate of MTBE is highly dependent on temperature and available dissolved oxygen concentration. Lower

temperatures were found to severely slow the rate of growth of a mixed culture, which under the best conditions was already slow. The culture was found to be more sensitive to low dissolved oxygen concentrations that typical heterotrophs which may be an important fact to consider in the design and operation of treatment or remediation systems. It was also shown that MTBE can inhibit the rate of benzene degradation which is an important fact to consider for in-situ bioremediation or natural attenuation of benzene contaminated groundwater which also contains MTBE.

Pavne, R.E., N.J. Novick, M.N. Gallagher

Pavne, R.E., N.J. Novick, M.N. Gallagher, 1997. Demonstrating intrinsic bioremediation of MTBE and BTEX in ground water at a service station site, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 418-419.

Using the ASTM first line of evidence, the character of both the MTBE and BTEX plumes at the site was evaluated. The MTBE plume remained stable and then disappeared, and the BTEX plume initially expanded, then shrank and then disappeared after four years of monitoring only. These observations indicate that the plume migration is being controlled by intrinsic bioremediation, which is consistent with other studies. However, under certain conditions, dissolved MTBE plumes can extend great distances. Work is in progress to characterize the conditions that affect these plumes.

Rong, Y.

Rong, Y. 1998. Soil Remedial Concentration for Methyl-Tertiary-Butyl-Ether by Monte Carlo Simulation Modeling, *in* The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998, [Proceedings]: Columbus, Ohio, Battelle Press, pp. 105-110.

This paper used Monte Carlo Simulation (MCS) for analysis of parameter uncertainties associated with a commonly used groundwater mixing model in a soil remediation case in Los Angeles, California, U.S.A. The mixing model is used in conjunction with a one-dimensional vadose zone transport model, VLEACH, to predict the impact of residual soil concentrations of MTBE on groundwater quality. Results of MCS can produce a probability distribution of model outputs. Such a statistical characterization would assist in decision making on soil remediation numerical criteria. The results of MCS demonstrate that model simulation based on a probabilistic approach could provide more information to decision makers than based on the conventional approach using single point average input values.

Rong, Y.

Rong, Y., 1998. Groundwater Data Analysis for Methyl Tertiary Butyl Ether in Los Angeles County and Ventura County: Ground Water Protection Council 1998 Annual Forum, September 19-23, 1998, Sacramento, CA, 8 p.

Based on data collected in Los Angeles Region, California, this paper summarizes MTBE concentration distribution in groundwater. MTBE groundwater data were correlated with concentrations of benzene, total petroleum hydrocarbons as gasoline (TPHg) in groundwater, and depth to groundwater. The correlation coefficient shows a poor correlation between MTBE and the above parameters. Also discussed is MTBE plume length and concentration changes over the distance of the plume length and over a period of monitoring time. The data show MTBE concentration decreases over the distance and increases over the time at the downgradient well. Findings of groundwater data analysis support our understanding that MTBE transport primarily depends upon its chemical properties, not upon other environmental factors. MTBE is the leading edge compound in the plume.

Salanitro, J.P., H.L. Wisniewski, I.J. Dortch

Salanitro, J.P., H.L. Wisniewski, I.J. Dortch, 1992. Effects of dissolved oxygen on biodegradation of gasoline components in saturated soil columns [abs.], *in* Abstracts of the 92nd general meeting of the American Society for Microbiology: American Society for Microbiology, v. 92, p. 354.

Salanitro, J., H. Wisniewski, P. McAllister

Salanitro, J., H. Wisniewski, P. McAllister, 1996. Observation on the biodegradation and bioremediation potential of methyl *t*-butyl ether [abs.], *in* Society of Environmental Toxicology and Chemistry abstract book, 17th, Washington, D.C., November 17-21, 1996: Washington, D.C., SETAC, p. 115.

There have been few reports documenting evidence for the biodegradation of the fuel oxygenate alkyl ether, methyl t-butyl ether (MTBE) in groundwater, soils, and biosludges. Partial (or complete) microbial breakdown of MTBE (e.g. to t-butyl alcohol, TBA) has been observed in an anaerobic subsoil (unsaturated clay), a river sediment under methanogenic conditions, a cyclohexane-degrading bacterial consortium and a pure culture of the methylotroph, Methylosinus trichosporium OB3b. An aerobic bacterial enrichment (BC-1) isolated from an industrial transient (non-accumulating metabolic intermediate. Our studies suggest that MTBE is cleaved by BC-1 to TBA which is then metabolized via isopropanol and acetone. There is little information on the occurrence of indigenous MTBE-degraders in groundwater, soils and activated sludges.

Preliminary evidence has been obtained, however, from a marketing terminal groundwater site that naturally occurring MTBE-degraders are present in some monitoring wells. Microcosm experiments with groundwater from this aquifer show that MTBE is aerobically degraded (no TBA formed) with a first-order decay rate (0.31/day) similar to BTEX. Also, MTBE (5,000-90,000 ppb) did not inhibit the intrinsic biodegradation potential of BTEX in groundwater microcosms. In summary, the data presented indicate that MTBE biodegradation has been observed in some environmental media. Further work is needed to assess the feasibility of using indigenous or derived aerobic or anaerobic MTBE-degrading cultures for treating fuel ethers in groundwaters or wastewater with in-situ or ex-situ bioremediation technologies.

Salanitro, J.P., L.A. Diaz, M.P. Williams, H.W. Wisniewski

Salanitro, J.P., L.A. Diaz, M.P. Williams, H.W. Wisniewski, 1994. Isolation of a bacterial culture that degrades methyl t-butyl ether: Applied and Environmental Microbiology, v. 60, no. 7, pp. 2593-2596.

A mixed bacterial culture (BC-1) has been isolated, which is capable of degrading the gasoline oxygenate MTBE. BC-1 was developed from seed microorganisms present in a chemical plant biotreater sludge. This enrichment culture has been maintained in continuous culture treating high concentrations of MTBE (120 to 200 mg/liter) as the sole carbon source in a simple feed containing NH_4^+, PO_4^{3-}, Mg^{+2}, CA^{+2}, nutrients. The unit had a stable MTBE removal rate when maintained with a long cell retention time (ca 80 to 90 days); however when operated at a $\leq$50-day cell waste rate, loss of MTBE-degrading activity was observed. The following three noteworthy experimental data show that MTBE is biodegraded extensively by BC-1: (i) the continuous (oxygen-sparred) culture was able to sustain a population of autotrophic ammonia-oxidizing bacteria which could nitrify influent NH_4^+ concentrations at high rates and obtain CO_2 (sole source for growth) from the metabolism of the alkyl ether, (ii) BC-1 metabolized radiolabeled either ($^{14}CH_3O$-MTBE) to $^{14}CO_2$ (40%) and ^{14}C-labeled cells (40%), and (iii) cell suspensions of the culture were capable of degrading (substrate depletion experiments) MTBE to *t*-butyl alcohol, a primary metabolite of MTBE. BC-1 is a mixed culture containing several bacterial species and is the first culture of its kind, which can completely degrade an alkyl ether.

Salanitro, J.P., Chi-Su Chou, H.L. Wisniewski, T.E. Vipond

Salanitro, J.P., Chi-Su Chou, H.L. Wisniewski, T.E. Vipond, 1998. Perspectives on MTBE biodegradation and the potential for in situ aquifer bioremediation, *in* The Southwest Focused Ground Water Conference--Discussing the Issue of MTBE and Perchlorate in Ground Water, Anaheim, Calif., June 3-4, 1998, [Proceedings]: Anaheim, Calif., National Ground Water Association, pp. 40-54.

Current knowledge of the microbial breakdown of the gasoline fuel oxygenate, MTBE, by soil and activated sludge culture enrichments indicate that: (1) microbial consortia can be isolated which metabolize MTBE via a pathway in which TBA is only a transient intermediate, (2) degrading cultures grow poorly and slowly on ethers, but metabolite accumulation is usually not observed, (3) biotreatment systems seeded with ether-degraders may be used to destroy MTBE in hydrocarbon-containing wastes (e.g. BTEX) and ground waters, but require longer hydraulic and biomass solids detention periods than conventional units, (4) the presence of indigenous MTBE-degraders in soil and groundwater is low and the enrichment of such plumes for natural attenuation would be limited given the low growth rate of these organisms, and (5) laboratory experiments on the inoculation of groundwater and aquifer sediments with ether-degrading cultures to enhance aerobic MTBE biodegradation suggest that aquifer seeding may be an approach for controlling the leading front of plumes. The stability, persistence and maintenance of ether-degrading activity in the biobarrier, however, remains to be evaluated in pilot-scale field tests.

Schirmer, M., J.F. Barker, C.E. Hubbard, C.D. Church, J.F. Pankow, P.G. Tratnyek

Schirmer, M., J.F. Barker, C.E. Hubbard, C.D. Church, J.F. Pankow, P.G. Tratnyek, 1997. The Borden field experiment--Where has the MTBE gone?, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 415-417.

This study investigates the fate of an MTBE plume introduced into the Canada Forces Base (CFB) Borden aquifer in order to quantify the long-term persistence of this contaminant in shallow, aerobic settings. MTBE was tracked in the aquifer for a 16–month period and compared to a conservative tracer. No measurable mass loss or retardation was observed within this time period. Eight years after injection of MTBE sampling was done to define the mass of the contaminate still present. It was expected that concentrations of MTBE would exceed 1000 μg/L but the highest hit was only 190 μg/L. Two possible explanations for the significant mass loss observed are that either the core segments of the plume have been missed or that MTBE has suffered significant mass loss over the last five years. No TBA or TBF has been found.

Schirmer, M. and Barker, J.F.

Schirmer, M., and Barker, J.F., 1998. A study of long-term MTBE attenuation in the Borden Aquifer, Ontario, Canada: Ground Water Monitoring & Remediation, Spring, pp. 113-122.

In 1988 and 1989, a natural gradient tracer test was performed in the shallow, aerobic sand aquifer a Canadian Forces Base (CFB) Borden. A mixture of groundwater containing dissolved oxygenated gasoline was injected below the water table along with chloride (Cl⁻) as a conservative

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Current knowledge of the microbial breakdown of the gasoline fuel oxygenate, MTBE, by soil and activated sludge culture enrichments indicate that: (1) microbial consortia can be isolated which metabolize MTBE via a pathway in which TBA is only a transient intermediate, (2) degrading cultures grow poorly and slowly on ethers, but metabolite accumulation is usually not observed, (3) biotreatment systems seeded with ether-degraders may be used to destroy MTBE in hydrocarbon-containing wastes (e.g. BTEX) and ground waters, but require longer hydraulic and biomass solids detention periods than conventional units, (4) the presence of indigenous MTBE-degraders in soil and groundwater is low and the enrichment of such plumes for natural attenuation would be limited given the low growth rate of these organisms, and (5) laboratory experiments on the inoculation of groundwater and aquifer sediments with ether-degrading cultures to enhance aerobic MTBE biodegradation suggest that aquifer seeding may be an approach for controlling the leading front of plumes. The stability, persistence and maintenance of ether-degrading activity in the biobarrier, however, remains to be evaluated in pilot-scale field tests.

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Schirmer, M., J.F. Barker, C.E. Hubbard, C.D. Church, J.F. Pankow, P.G. Tratnyek, 1997. The Borden field experiment--Where has the MTBE gone?, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 415-417.

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Schirmer, M., J.F. Barker, C.E. Hubbard, C.D. Church, J.F. Pankow, P.G. Tratnyek, 1997. The Borden field experiment--Where has the MTBE gone?, *in* American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, Calif.: ACS, v. 37, no. 1, pp. 415-417.

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Schirmer, M. and Barker, J.F.

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In 1988 and 1989, a natural gradient tracer test was performed in the shallow, aerobic sand aquifer a Canadian Forces Base (CFB) Borden. A mixture of groundwater containing dissolved oxygenated gasoline was injected below the water table along with chloride (Cl⁻) as a conservative

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tracer. The migration of BTEX, MTBE, and Cl⁻ was monitored in detail for 16 months. The mass of BTEX compounds in the plume diminished significantly with time due to intrinsic aerobic biodegradation, while MTBE showed only a small decrease in mass over the 16-month period. In 1995/96, a comprehensive ground water sampling program was undertaken to define the mass of the MTBE still present in the aquifer. Since the plume had migrated into an unmonitored section of the Borden Aquifer, numerical modeling and geostatistical methods were applied to define an optimal sampling grid and to improve the level of confidence in the result. A drive point profiling system was used to obtain groundwater samples. Numerical modeling with no considerations in excess of 3000 ppb; field sampling found maximum concentration found maximum concentrations of less than 200 ppb. A mass balance for the remaining MTBE mass in the aquifer eight years after injection showed that only 3% of the original mass remained. Sorption, volatilization, abiotic degradation, and plant uptake are not considered significant attenuation processes for the field conditions. Therefore, it is suggested that biodegradation may have played a major role in the attenuation of MTBE within the Borden Aquifer.

Schirmer, M., J.F. Barker, B.J. Butler, C.D. Church, K.S. Schirmer

Schirmer, M., J.F. Barker, B.J. Butler, C.D. Church, K.S. Schirmer, 1998. Natural Attenuation of MTBE at the Borden Field Site: The First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998, Proceedings: Columbus, Ohio, Battelle Press, pp. 327-331

A natural gradient tracer test was performed in the shallow, aerobic sand aquifer at Canadian Forces Base (CFB) Borden in 1988. A mixture of groundwater containing dissolved oxygenate-containing gasoline was injected below the water table along with chloride (Cl⁻) as a conservative tracer. The mass of BTEX compounds in the plume diminished significantly with time due to intrinsic aerobic biodegradation; MTBE showed only a small decrease in mass over the 16-month period. In 1995/96, a comprehensive ground water sampling program was undertaken to define the mass of MTBE still present in the aquifer. Only 3% of the original MTBE mass remained. Sorption, volatilization and abiotic degradation were ruled out as significant attenuation processes for the field conditions. As well, a study of the phytoremediation potential of the site showed that the plants in the study area did not contribute to the disappearance of the MTBE mass. These results indicate that biodegradation may have played a major role in the attenuation of MTBE within the Borden aquifer. In support of this hypothesis, significant MTBE mass losses were observed over the first 110 days in an ongoing aerobic laboratory batch experiment that uses authentic Borden aquifer material and ground water. Therefore, it appears that MTBE, like BTEX, can be remediated intrinsically due to biodegradation. Unlike BTEX, however, MTBE is biodegraded very slowly making biodegradation likely insufficient in protecting aquifers and downgradient receptors once MTBE is spilled at a site.

Squillace, P.J.

Squillace, P.J., 1996. A review of the environmental behavior and fate of fuel oxygenates [abs.], *in* Society of Environmental Toxicology and Chemistry abstract book, 17th, Washington, D.C., November 17-21, 1996: Washington, D.C., SETAC, pp. 114-115.

The ways in which fuel oxygenate compounds behave in water, soil, and air are determined by how they partition among the different media. The behavior of a gasoline oxygenate in water is affected by the oxygenate's (1) solubility in water from gasoline; (2) partitioning between water and soil materials; and (3) partitioning between air and water. Water in equilibrium with oxygenated gasoline can contain high concentrations of the oxygenate. For example, at room temperature water solubility of MTBE will be about 5000 mg/L for a gasoline that is 10% MTBE by weight. In contrast, the total hydrocarbon solubility in water is typically about 120 mg/L for non-oxygenated gasoline. Fuel oxygenates sorb only weakly to soil and aquifer materials. Therefore, sorption to these materials will not significantly retard their transport by groundwater. Fuel oxygenates tend to partition into atmospheric water, including precipitation. For example, washout of gas-phase MTBE by precipitation would not, by itself, greatly alter the gas-phase concentration of the compound in the atmosphere. Nevertheless, the partitioning of MTBE to precipitation is strong enough to allow for submicrogram per liter to 3 μg/L or more inputs of MTBE to groundwater and surface water. Occurrence data for MTBE in water and air supports partition theoretical calculations. MTBE and other alkyl ether oxygenates have half lives in the atmosphere that range from 1 to 14 days. These compounds are generally considered recalcitrant in groundwater; whereas ethanol and methanol will readily undergo microbial degradation except where present in concentrations toxic to microorganisms.

Squillace, P.J., J.F. Pankow, J.S. Zogorski

Squillace, P.J., J.F. Pankow, J.S. Zogorski, 1998. Environmental behavior and fate of methyl *tert*-butyl ether (MTBE), *in* The Southwest Focused Ground Water Conference--Discussing the Issue of MTBE and Perchlorate in Ground Water, Anaheim, Calif., June 3-4, 1998 [Proceedings]: Anaheim, Calif., National Ground Water Association, pp. 4-9.

When gasoline that has been oxygenated with MTBE comes in contact with water, large amounts of MTBE can dissolve; at 25 degrees Celsius the water solubility of MTBE is about 5000 mg/L for a gasoline that is 10% MTBE by weight. In contrast, for a nonoxygenated gasoline, the total hydrocarbon solubility in water is typically about 120 mg/L. MTBE sorbs only weakly to soil and aquifer materials; therefore, sorption will not significantly retard MTBE's transport by ground water. In addition, MTBE generally resists degradation in ground water. The half-life of MTBE in the atmosphere can be as short as 3 days in a regional airshed. MTBE in the air tends to partition

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into atmospheric water, including precipitation. However, washout of gas-phase MTBE by precipitation is nevertheless strong enough to allow for up to 3 micrograms per liter or more inputs of MTBE to surface and groundwater.

Squillace, P.J., J.S. Zogorski, W.G. Wilber, C.V. Price

Squillace, P.J., J.S. Zogorski, W.G. Wilber, C.V. Price, 1996. Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1994, USGS Open File Report OFR 95-456, U.S. Geological Survey, Rapid City, South Dakota, 16 p.

Out of 60 volatile organic chemicals analyzed, MTBE was the most frequently detected chemical in samples of shallow ambient ground water from urban areas that were collected during 1993-94 as part of the U.S. Geological Survey's National Water-Quality Assessment program. Samples were collected from 5 drinking-water wells, 12 springs, and 193 monitoring wells in urban areas. No MTBE was detected in drinking water wells. At a reporting level of 0.2 μg/L, MTBE was detected most frequently in shallow ground water from urban areas (27% of 210 wells and springs sampled in 8 areas) as compared to shallow groundwater from agricultural areas (1.3% of 549 wells sampled in 21 areas) or deeper ground water from major aquifers (1% of 412 wells sampled in 9 areas). Only 3% of the shallow wells sampled in urban areas had concentrations of MTBE that exceeded 20 μg/L, which is the estimated lower limit of the U.S. Environmental Protection Agency draft drinking-water health advisory. Because MTBE is persistent and mobile in groundwater, it can move from shallow to deeper aquifers with time. In shallow urban groundwater, MTBE generally was not found with benzene, toluene, ethyl-benzene, or xylenes (BTEX) compounds which is commonly are associated with gasoline spills. This disassociation causes uncertainty as to the source of MTBE. Possible sources of MTBE in ground water include point sources, such as LUSTs, and non-point sources, such as recharge of precipitation and storm-water runoff.

Squillace, P.J., J.F. Pankow, N.E. Korte, J.S. Zogorski

Squillace, P.J., J.F. Pankow, N.E. Korte, J.S. Zogorski, 1996. Environmental behavior and fate of methyl *tert*-butyl ether (MTBE): U.S. Geological Survey Fact Sheet FS-203-96, 6 p.

When gasoline that has been oxygenated with MTBE comes in contact with water, large amounts of MTBE can dissolve; at 25 degrees Celsius the water solubility of MTBE is about 5,000 milligrams per liter for a gasoline that is 10% MTBE by weight. In contrast, for an non-oxygenated gasoline, the total hydrocarbon solubility in water is typically about 120 milligrams per liter. MTBE sorbs only weakly to soil and aquifer materials; therefore, sorption will not significantly retard MTBE's transport by groundwater. In addition, MTBE generally resists

degradation groundwater. The half-life of MTBE in the atmosphere can be as short as 3 days in a regional airshed. MTBE in the air tends to partition into atmospheric water, including precipitation. However, washout of gas-phase MTBE by precipitation would not, by itself, greatly alter the gasphase concentration of the compound in the air. The partitioning of MTBE to precipitation is nevertheless strong enough to allow for up to 3 micrograms per liter or more inputs of MTBE to surface and groundwater.

Steffan, R.J., K. McClay, S. Vainberg, C.W. Condee, D. Zhang

Steffan, R.J., K. McClay, S. Vainberg, C.W. Condee, D. Zhang, 1997. Biodegradation of the Gasoline Oxygenates Methyl tert-Butyl Ether, Ethyl Ether, and tert-Amyl Methyl Ether by Propane-Oxidizing Bacteria: Applied and Environmental Microbiology, v. 63, no. 11, pp. 4216-4222.

Several propane-oxidizing bacteria were tested for their ability to degrade gasoline oxygenates, including MTBE, ETBE, and TAME. Both a laboratory strain and natural isolates were able to degrade each compound after growth on propane. When propane-grown strain ENV425 was incubated with 20 mg of uniformly labeled [^{14}C] MTBE per liter, the strain converted >60% of the added MTBE to $^{14}CO_2$ in <30 h. The initial oxidation of MTBE and ETBE was oxidized to formaldehyde and ultimately CO_2. TBA was further oxidized to 2-methyl-2-dydroxy-1-propanol and then 2-hydroxy isobutyric acid; however, neither of these degradation products was an effective growth substrate for the propane oxidizers. Analysis of cell extracts of ENV425 and experiments with enzyme inhibitors implicated a soluble P-450 enzyme in the oxidation of both MTBE and TBA. MTBE was oxidized to TBA by camphorgrown *Pseudomonas putida* CAM, which produces the well-characterized P-450cam, but not by *Rhodococcus rhodochrous* 116, which produces two P-450 enzymes. Rates of MTBE degradation by propane-oxidizing strains ranged from 3.9 to 9.2 nmol/min/mg of cell protein at 28°C, whereas TBA was oxidized at a rate of only 1.8 to 2.4 nmol/min/mg of cell protein at the same temperature.

Suflita, J.M., and Mormile, M.R.

Suflita, J.M., and Mormile, M.R., 1993. Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface: Environmental Science & Technology, v. 27, no. 5, pp. 976-978.

This paper has three areas of discussion. Known and potential gasoline oxygenates are examined for their susceptibility to anaerobic decay. Structural features that tended to favor or retard the anaerobic destruction of these materials are identified. Potential gasoline oxygenates which may be more environmentally acceptable that the additives currently employed are identified. Degradation of the oxygenates was done in laboratory slurries comprised of 75 mL of

groundwater and 50g of sediment collected from a methanogenic portion of a shallow aquifer polluted by municipal landfill leachate. An oxygenate concentration of 50 ppm C was used. Results indicated no evidence for anaerobic destruction of tert-butyl alcohol (TBA). After at least 182 days, no evidence for the anaerobic destruction of MTBE could be obtained.

Truong, K.N., and Parmele, C.S

Truong, K.N., and Parmele, C.S., 1992. Cost-effective alternative treatment technologies for reducing the concentrations of methyl tertiary butyl ether and methanol in groundwater, *in* Calabrese, E.J. and Kostecki, P.T., eds.: Hydrocarbon contaminated soils and groundwater, v. 2: Chelsea, Mich., Lewis Publishers, Inc., pp. 461-486.

Describes an engineering assessment of eight treatment technologies conducted by IT Corporation for the American Petroleum Institute for removing MTBE or methanol and benzene, toluene, xylene (BTX) in three following groundwater treatment scenarios:

- Removal of MTBE to 10 ppb by eight technologies

- Removal of methanol to 100 ppb by four selected technologies

- Removal of methanol to 1,000 ppb by two selected technologies at several combinations of BTX inlet concentrations and flow rates.

The following eight technologies were evaluated for removing 20 ppm of MTBE from groundwater that also contained 20-ppm total BTX:

- Air stripping with aqueous-phase carbon adsorption

- Air stripping with off-gas incineration and aqueous-phase carbon adsorption

- Air stripping alone

- Heated air stripping

- Steam stripping

- Diffused aeration

- Aboveground biological treatment

- Ultraviolet (UV)-catalyzed oxidation using hydrogen peroxide (H_2O_2) and ozone (O_3)

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Tyner, L., K. Brown, D. Caron, T. Perina, D. Daftary, B. Sibbett

Tyner, L., K. Brown, D. Caron, T. Perina, D. Daftary, B. Sibbett, 1998. Natural Attenuation of BTEX and MTBE Under Complex Hydrogeological Conditions, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, California, May 18-21, 1998, Proceedings: Columbus, Ohio, Battelle Press, pp. 333-339.

Natural attenuation was evaluated for containment of gasoline-impacted, shallow, perched groundwater at Vandenberg AFB Base Exchange Service Station. The BTEX and MTBE plume resulted from leaking USTs, which had been replaced. The field effort focused on development of a site conceptual model, delineation of the containment plume, and natural attenuation and phytoremediation data. Initial modeling efforts included the impact of groundwater movement due to uptake by the existing on-site eucalyptus trees. Overall, the biocapacity of the aquifer to assimilate the release exceeded the sum BTEX detected and although contaminants may persist at the site for an extended period of time, no off-site migration of the MTBE or BTEX plume was identified. The BTEX attenuation time to achieve 1 ppb was estimated at less than 100 years; MTBE concentrations persisted at the site, with the maximum concentrations occurring in the vicinity of the Eucalyptus trees.

U.S. Environmental Protection Agency

U.S. Environmental Protection Agency, 1997. Fact Sheet -Drinking Water Advisory-- Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE): Washington, D.C., Office of Water, EPA-822-F-97-009, 4 p.

The EPA has issued a drinking water advisory for MTBE. It was concluded that keeping concentrations in the range of 20 to 40 μg/L will likely avert unpleasant taste and odor effects, recognizing that some people may detect the chemical below this. There are no data on the effects on humans of drinking MTBE-contaminated water. In laboratory tests on animals, cancer and non-cancer effects occur at high levels of exposure. Advisories are not mandatory standards for action. Advisories are used only for guidance and are not legally enforceable.

U.S. Environmental Protection Agency

U.S. Environmental Protection Agency, 1998. MTBE Fact Sheet #1 – Overview, Washington, D.C., Office of Underground Storage Tanks, EPA-510-F-97-014, January, 5 p.

Provides background information on MTBE and health concerns arising from its presence in soil and groundwater

U.S. Environmental Protection Agency

U.S. Environmental Protection Agency, 1998. MTBE Fact Sheet #2 – Remediation of Contaminated Soil and Groundwater, Washington, D.C., Office of Solid Waste and Emergency Response, EPA-510-F-97-015, January, 5 p.

Remediating MTBE contaminated groundwater can be problematic. MTBE's high solubility in water, low rate of adsorption to soil, and low rate of biodegradation can make treating groundwater contaminated with MTBE more expensive than treating groundwater contaminated with petroleum that does not contain MTBE. Fortunately, there are proven treatment technologies available. Pump and treat is usually the most cost-effective method, but in some cases air sparging may be appropriate. Other existing technologies may also prove effective as more case studies are reported. The potential for *in situ* biodegradation of MTBE is widely believed to be low, but new research may clarify our understanding of conditions that may make it an effective option. In addition to remediation of the source area, point-of-use treatment appears to be a common approach to addressing MTBE when contamination is limited to individual homes or private wells.

U.S. Environmental Protection Agency

U.S. Environmental Protection Agency, 1998. MTBE Fact Sheet #3 –Use and Distribution of MTBE and Ethanol, Washington, D.C., Office of Underground Storage Tanks, EPA-510-F-97-016, January, 3 p.

MTBE is preferred by the petroleum refinery industry over ethanol for octane enhancement and RFG (2.0 % oxygen, all year) because it is less expensive, is easier to use, and creates a gasoline with a lower vapor pressure. Although MTBE is also used in winter months, ethanol is commonly used in Oxyfuel (2.7 % oxygen in fall/winter months) because government subsidies make it price competitive and because gasoline volatility is not a major concern in cold weather. Although these trends in the use and distribution of oxygenated fuels are useful in helping to determine what type of additive to expect in a region, they are not predictive. MTBE may be found in new or old releases in virtually all areas of the United States

U.S. Environmental Protection Agency

U.S. Environmental Protection Agency, 1998. Seminars on Monitored Natural Attenuation for Ground Water, Washington, D.C., Office of Research and Development, EPA/625/K-98/001, September.

Provides and overview of Monitored Natural Attenuation (MNA). Covers trends in the use of MNA, Framework for use of MNA, biological and geochemical context for MNA, how hydrogeology affects the efficiency of natural attenuation, the estimation of biodegradation and

attenuation rate constants, risk management of MNA, and sampling, analysis and monitoring to evaluate MNA. Also presented are case studies of MTBE natural attenuation in groundwater. Sites include: U.S. Coast Guard Support Center and Fire Station Spill in Elizabeth City, N.C., the Borden Aquifer experiment, and sites in Patchogue, NY, and Sampson N.C.

Wagler, J.L. and Malley Jr., J.P.

Wagler, J.L. and Malley Jr., J.P., 1994. The Removal of Methyl Tertiary-Butyl Ether from a Model Ground Water Using UV/Peroxide Oxidation: Journal of the New England Water Works Association, September, pp. 236-243.

This paper explores the alternative oxidation processes of UV photolysis, hydrogen peroxide (H_2O_2), and the combination of UV/ H_2O_2 to remove MTBE from model groundwater. The UV/ H_2O_2 process removed MTBE to draft health advisory levels in less than two hours. Since this process was effective, studies were run to determine the most efficient pH range and the effects of varying the molar ratio of MTBE to H_2O_2. The results indicated the reaction was pseudo first order, but the rate was slower than the model water rate at pH 8.0. An analysis of an MTBE sample that was not completely oxidized suggested that methanol is a major intermediate and/or byproduct of the UV/ H_2O_2 process along with trace amounts of formaldehyde and 1,1-dimethyl ethyl formate. UV/ H_2O_2 oxidation of an actual groundwater containing MTBE and other volatile organic chemical produced 83% removal of MTBE after two hours of exposure.

Weaver, J.W., J.E. Haas, J.T. Wilson

Weaver, J.W., J.E. Haas, J.T. Wilson, 1996. Analysis of the Gasoline Spill at East Patchoque, New York: Accepted for the Proceedings of the American Society of Civil Engineers Conference on Non-aqueous Phase Liquids in the Subsurface Environment: Assessment and Remediation, Nov. 12-14, 1996 Washington, D.C. 12 p.

Gasoline containing MTBE was released from a service station in East Patchoque, Long Island, New York. The resulting plume of contaminated groundwater was over 1800 m (6000 ft) long, and resulted in the closing of private water supply wells. Data from a three-dimensional monitoring network were used to estimate the mass and position of the center of mass of benzene, toluene, ethylbenzene, xylenes, and MTBE contaminant plumes. The monitoring network was sampled on three occasions so temporal information on the evolution of the plume was available. By estimating the moments of the contaminant distributions for each of the sample rounds, the loss of mass of each contaminant was estimated, as was the rate of migration of the center of mass. An estimate of the volume of gasoline released was made from plausible estimates of the gasoline composition.

Yeh, C.K., and Novak, J.T.

Yeh, C.K., and Novak, J.T., 1991. Anaerobic biodegradation of oxygenates in the subsurface, *in* NWWA/API Petroleum Hydrocarbons and Organic Chemicals in Ground Water--Prevention, Detection, and Restoration, Houston, Tex., November 20-22, 1991, Book 8 [Proceedings]: Houston, Tex., National Water Well Association and American Petroleum Institute, pp. 427-441.

Yeh, Kuei-Jyum

Yeh, Kuei-Jyum, 1992. Degradation of Gasoline Oxygenates in the Subsurface: Ph.D. dissertation, Virginia Polytechnic Institute and State Univ., Blacksburg.

Biodegradation was evaluated in static soil/water microcosms. Aquifer material was collected from various depths at three sites with different soil characteristics. Potential electron acceptors including O_2 in the form of H_2O_2, nitrate or sulfate was added to induce the desired metabolism (aerobic respiration, denitrification, sulfate reduction, or methanogenesis). In each metabolic process, the influence of several subsurface environmental factors on biodegradation was investigated.

The data show that biodegradation potential of MTBE, ETBE and TBA varied substantially with site and depth. TBA was the easiest compound to biodegrade, whereas MTBE was the most recalcitrant. Cleavage of the ether bond is the first and rate-limiting step in the degradation of ETBE and possibly MTBE.

Addition of H_2O_2 caused chemical oxidation of MTBE and ETBE. The chemical oxidation was faster in the organically rich soils, but slower in the organic-poor soils. Soil microorganisms were able to catalyze the cleavage of the ether bond in ETBE but not MTBE. This biological reaction was not significant when chemical oxidation occurred. TBA, on the other hand, was aerobically biodegraded in all soils.

Under denitrifying and anaerobic conditions TBA degradation occurred in all soils but the degradation of ETBE and MTBE was only observed at one of three sites. TBA degradation was enhanced by nutrient addition in the nutrient-poor soil but hindered by the presence of the other easily degraded organic compounds. Degradation of MTBE and ETBE was observed in the organic-rich soils and in the organically poor soils, the addition of ethanol inhibited MTBE and ETBE degradation.

Yeh, C.K., and Novak, J.T.

Yeh, C.K., and Novak, J.T., 1994. Anaerobic biodegradation of gasoline oxygenates in soils: Water Environment Research, v. 66, no. 5, pp. 744-752.

This study evaluated the biodegradation of methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary butyl alcohol (TBA) – three chemicals used as gasoline additives. The biodegradation under sulfate reducing, methanogenic and denitrifying conditions was measured in static soil and water microcosms using soils of different origin and varying characteristics. The results indicate that TBA was the easiest compound to biodegrade, whereas MTBE was the most recalcitrant. It is thought that cleavage of the ether bond in MTBE and ETBE is the first and rate-limiting step in the degradation of these organics. TBA degradation was enhanced by nutrient addition in the nutrient poor soils but hindered by the presence of other easily degraded organic compounds. Degradation of MTBE and ETBE occurred only in the soil with the lowest organic matter content and with a pH around 5.5. No degradation of MTBE and ETBE was observed in the organic rich soils, and in the organically poor soil the addition of easily degradable organic compounds inhibited MTBE and ETBE degradation.

Yeh, C.K., and Novak, J.T.

Yeh, C.K., and Novak, J.T., 1995. The effect of hydrogen peroxide on the degradation of methyl and ethyl *tert*-butyl ether in soils: Water Environment Research, v. 67, no. 5, pp. 828-834.

The degradation of the gasoline oxygenates, MTBE, ETBE, in soil systems was evaluated. The data indicated that MTBE and ETBE were chemically oxidized to tertiary butanol and acetone when H_2O_2 was added to soil microcosms containing aquifer material from an organic rich site. Identical reactions were observed when H_2O_2 was added to solutions containing soluble ferrous iron and either MTBE or ETBE. Chemical oxidation was influenced by the H_2O_2 concentration, pH, and the presence of ferrous iron but was independent of the iron concentration. Naturally occurring aerobic microcosms in the soil were able to degrade ETBE but not MTBE. Chemical oxidation coupled with an aerobic-anaerobic-biological cycle is proposed to describe a degradation pathway for ETBE in H_2O_2 amended soils.

Zogorski, J.S., A.L. Baehr, B.J. Bauman, D.L. Conrad, R.T. Drew, N.E. Korte, W.W. Lapham, A. Morduchowitz, J.F. Pankow, E.R. Washington

Zogorski, J.S., A.L. Baehr, B.J. Bauman, D.L. Conrad, R.T. Drew, N.E. Korte, W.W. Lapham, A. Morduchowitz, J.F. Pankow, E.R. Washington, 1997. Significant Findings and Water-Quality Recommendations of the Interagency Oxygenated Fuel Assessment, *in* The Seventh Annual West Coast Conference on Contaminated Soils and Groundwater, Oxnard, CA, March 10-13, 1997, [Proceedings]: Amherst, MA, Association for the Environmental Health of Soils, pp. 1-22.

This paper summarizes significant findings and water-quality recommendations of the Interagency Oxygenated Fuel Assessment reported in Zogorski et al., 1997. The Assessment addresses water-quality issues arising from the production, distribution, storage, and use of fuel

oxygenates and their movement in the hydrologic cycle. It summarizes the scientific literature, data, and agency information on the sources, concentrations, behavior, and fate of fuel oxygenates and their aqueous degradation products in ground water and in surface water.

Zogorski, J.S., G.C. Delzer, D.A. Bender, P.J. Squillace, T.J. Lopes, A.L. Baehr, P.E. Stackelberg, J.E. Landmeyer, C.J. Boughton, M.S. Lico, J.F. Pankow, R.L. Johnson, N.R. Thomson

Zogorski, J.S., G.C. Delzer, D.A. Bender, P.J. Squillace, T.J. Lopes, A.L. Baehr, P.E. Stackelberg, J.E. Landmeyer, C.J. Boughton, M.S. Lico, J.F. Pankow, R.L. Johnson, N.R. Thomson, 1998. MTBE--Summary of findings and research by the U.S. Geological Survey, *in* 1998 Annual Conference of Water Quality, Atlanta, Ga. [Proceedings]: American Water Works Association (in press).

Much of the USGS's MTBE monitoring and research is in a formative stage and few definitive conclusions have been reached at this time. However, several preliminary observations are noteworthy. First, ambient water-quality monitoring in the National Water-Quality Assessment (NAWQA) Program indicates frequent detection of MTBE in stormwater, small streams, and shallow groundwater in those cities and metropolitan areas where MTBE is used extensively in gasoline. For example, of 60 volatile organic compounds (VOCs) for which water samples are commonly analyzed, MTBE is the second most frequently detected VOC in shallow ground water in urban areas, with a detection frequency of 27 percent. However, 97 percent of the detections are at concentrations below the USEPA drinking-water advisory. Second, because monitoring in the NAWQA Program is not targeted to point source gasoline release sites or to effluent-dominated streams, most of the low-level detections of MTBE are thought to originate from non-point sources. Land surfaces and the atmosphere appear to be plausible non-point sources of MTBE to urban water resources. Admittedly, point sources located at some distance from sampled wells may also be a source. Third, MTBE has been detected at low levels in 14 percent of urban wells sampled from aquifers used for drinking water. In contrast, 2 percent of rural wells sampled from drinking-water aquifers contain MTBE. Lastly, concentrations of MTBE in ground water contaminated by a gasoline storage-tank release that occurred in the mid-1980s remain high and above the USEPA's drinking water advisory. Furthermore, observed decreases in MTBE concentrations in ground water observed since 1993, when monitoring was begun at the site, are attributed primarily to abiotic processes of natural attenuation including dilution by mixing and some volatilization. Biodegradation is not a major attenuation process at this site.

Zogorski, J.S., A. Morduchowitz, A.L. Baehr, B.J. Bauman, D.L. Conrad, R.T. Drew, N.E. Korte, W.W. Lepham, J.F. Pankow, E.R. Washington

Zogorski, J.S., A. Morduchowitz, A.L. Baehr, B.J. Bauman, D.L. Conrad, R.T. Drew, N.E. Korte, W.W. Lepham, J.F. Pankow, E.R. Washington, 1997. Fuel oxygenates and water quality: Current Understanding of Sources, occurrence in Natural Waters, Environmental Behavior, Fate, and Significance; Executive Office of the President, Office of Science and Technology Policy: Washington D.C.

Provides extensive information on physical and chemical characteristic of MTBE as well as fate in the environment.

APPENDIX B

**PARTICIPATION IN OXYFUELS AND RFG PROGRAMS, MTBE
CONTENT OF REPRESENTATIVE GASOLINES, AND STATE
REGULATIONS DEALING WITH MTBE**

APPENDIX B1

FEDERAL REFORMULATED GASOLINE (RFG) PROGRAM AREAS

APPENDIX B1

FEDERAL REFORMULATED GASOLINE (RFG) PROGRAM AREAS

US Environmental Protection Agency, Office of Mobile Sources
List of Federal Reformulated Gasoline Program Areas[a]
July 2, 1998

Clean Air Act
REQUIRED AREAS
LOS ANGELES - South Coast Air Basin, South East Desert, Ventura, CA
-          Los Angeles County, CA
-          Ventura County, CA
-          Orange County, CA
-          San Bernardino County (partial), CA
-          Riverside County (partial), CA

SAN DIEGO County, CA
-          San Diego County, CA

HARTFORD - New Haven - Waterbury, CT
-          Hartford County (partial), CT
-          Litchfield County (partial), CT
-          Middlesex County (partial), CT
-          New London County (partial), CT
-          New Haven County (partial), CT
-          Tolland County (partial), CT

NEW YORK - Northern New Jersey - Long Island - Connecticut area, NY-NJ-CT
-          Fairfield County, CT
-          Litchfield County, (partial), CT
-          New Haven County (partial), CT
-          Bergen County, NJ
-          Essex County, NJ
-          Hudson County, NJ
-          Hunterdon County, NJ
-          Middlesex County, NJ
-          Monmouth County, NJ
-          Morris County, NJ
-          Ocean County, NJ
-          Passaic County, NJ
-          Somerset County, NJ
-          Sussex County, NJ
-          Union County, NJ
-          Bronx County, NY
-          Kings County, NY
-          Nassau County, NY
-          New York County, NY
-          Orange County, NY
-          Putnam, NY
-          Queens County, NY
-          Richmond County, NY
-          Rockland County, NY
-          Suffolk County, NY
-          Westchester County, NY

PHILADELPHIA - Wilmington - Trenton - Cecil County, MD area PA-NJ-DE-MD
- New Castle County, DE
- Kent County, DE
- Cecil County, MD
- Burlington County, NJ
- Camden County, NJ
- Cumberland County, NJ
- Gloucester County, NJ
- Mercer County, NJ
- Salem County, NJ
- Bucks County, PA
- Chester County, PA
- Delaware County, PA
- Montgomery County, PA
- Philadelphia County, PA

CHICAGO - Gary - Lake County, IL - Indiana - Wisconsin area
- Cook County, IL
- Du Page County, IL
- Kane County, IL
- Lake County, IL
- McHenry County, IL
- Will County, IL
- Grundy County, IL, (partial)
- Kendall County, IL,(partial)
- Lake County, IN
- Porter County, IN

BALTIMORE, MD
- Anne Arundel County, MD
- Baltimore County, MD
- Carroll County, MD
- Harford County, MD
- Howard County, MD
- The City of Baltimore, MD

HOUSTON - Galveston - Brazoria, TX
- Brazoria County, TX
- Chambers County, TX
- Fort Bend County, TX
- Galveston County, TX
- Harris County, TX
- Liberty County, TX
- Montgomery County, TX
- Waller County, TX

MILWAUKEE - Racine, WI
- Kenosha County, WI
- Milwaukee County, WI

-     Ozaukee County, WI
-     Racine County, WI
-     Washington County, WI
-     Waukesha County, WI

SACRAMENTO, CA [*] (newly required area)
-     El Dorado County (partial), CA
-     Placer County (partial), CA
-     Sacramento County, CA
-     Solano County (partial), CA
-     Sutter County (partial), CA
-     Yolo County, CA

* Reclassification of Sacramento from Serious to Severe was effective June 1, 1995. RFG was required as of June 1, 1996.

"OPT-IN" AREAS (Voluntary)
CONNECTICUT, The Entire State [b/]
-          Litchfield County (partial), CT
-          Hartford County (partial), CT
-          Middlesex County (partial), CT
-          New London County (partial), CT
-          Tolland County (partial), CT
-          Windham County, CT

DELAWARE, The Entire State [b/]
  Sussex nonattainment area
-          Sussex County, DE

DISTRICT OF COLUMBIA
  Washington, DC-MD-VA area (DC portion)
-          Entire District of Columbia

KENTUCKY
  Cincinnati-Hamilton KY-OH area (KY portion)
-          Boone County, KY
-          Campbell County, KY
-          Kenton County, KY
  Louisville, KY-IN area (KY portion)
-          Jefferson County, KY
-          Bullitt County (partial), KY
-          Oldham County (partial), KY

MAINE
  Knox & Lincoln nonattainment area
-          Knox County, ME
-          Lincoln County, ME
  Lewiston-Auburn nonattainment area
-          Androscoggin County, ME
-          Kennebec County, ME
  Portland nonattainment area
-          Cumberland County, ME
-          Sagadahoc County, ME
-          York County, ME

MARYLAND
  Washington, DC-MD-VA area (MD portion)
-          Calvert County, MD
-          Charles County, MD
-          Frederick County, MD
-          Montgomery County, MD
-          Prince Georges County, MD
  Kent & Queen Anne's nonattainment area
-          Queen Anne's County, MD
-          Kent County, MD

MASSACHUSETTS, The Entire State [b/]
   Boston-Lawrence-Worcester (E. MA)
- Barnstable County, MA
- Bristol County, MA
- Dukes County, MA
- Essex County, MA
- Middlesex County, MA
- Nantucket County, MA
- Norfolk County, MA
- Plymouth County, MA
- Suffolk County, MA
- Worcester County, MA

Springfield (Western MA) nonattainment areas
- Berkshire County, MA
- Franklin County, MA
- Hampden County, MA
- Hampshire County, MA

NEW HAMPSHIRE
   Boston-Lawrence-Worcester, MA-NH nonattainment area   (NH portion)
- Hillsborough County, NH
- Rockingham County, NH
- Merrimack County, NH
- Strafford County, NH

NEW JERSEY, The Entire State [b/]
   Allentown-Bethlehem-Easton area (NJ portion)
- Warren County, NJ
   Atlantic City nonattainment area
- Atlantic County, NJ
- Cape May County, NJ

NEW YORK
   Essex nonattainment area
- Dutchess County, NY
- Essex County (partial), NY

RHODE ISLAND, The Entire State [1]
   Providence nonattainment area
- Bristol County, RI
- Kent County, RI
- Newport County, RI
- Providence County, RI
- Washington County, RI

TEXAS
Dallas-Fort Worth nonattainment area
-              Collin County, TX
-              Dallas County, TX
-              Denton County, TX
-              Tarrant County, TX

VIRGINIA
Washington DC-MD-VA area (VA portion)
-              Alexandria, VA
-              Arlington County, VA
-              Fairfax, VA
-              Fairfax County, VA
-              Falls Church, VA
-              Loudoun County, VA
-              Manassas, VA
-              Manassas Park, VA
-              Prince William County, VA
-              Stafford County, VA
Richmond, VA nonattainment area
-              Charles City County, VA
-              Chesterfield County, VA
-              Colonial Heights, VA
-              Hanover County, VA
-              Henrico County, VA
-              Hopewell, VA
-              Richmond, VA
Norfolk-Virginia Beach-Newport News area
-              Chesapeake, VA
-              Hampton, VA
-              James City County, VA
-              Newport News, VA
-              Norfolk, VA
-              Poquoson, VA
-              Portsmouth, VA
-              Suffolk, VA
-              Virginia Beach, VA
-              Williamsburg, VA
-              York County, VA.

Opt-Out Areas

Note: *These "Opt-Out" areas withdrew from the federal RFG program before it went into effect on January 1, 1995. See below for details.*

MAINE

Hancock and Waldo Counties, ME
- Hancock County
- Waldo County

PENNSYLVANIA

Allentown - Bethlehem - Easton, PA
- Carbon County
- Lehigh County
- Northampton County

Altoona, PA
- Blair County

Erie, PA
- Erie County

Harrisburg - Lebanon - Carlisle, PA
- Cumberland County
- Dauphin County
- Lebanon County
- Perry County

Johnstown, PA
- Cambria County
- Somerset County

Lancaster, PA
- Lancaster County

Pittsburgh - Beaver Valley, PA
- Allegheny County
- Beaver County
- Fayette County
- Washington County
- Westmoreland County
- Armstrong County
- Butler County

Reading, PA
- Berks County

Scranton - Wilkes-Barre, PA
- Columbia County
- Lackawanna County
- Luzerne County
- Monroe County
- Wyoming County

York, PA
- Adams County
- York County

Youngstown, OH - Warren, OH - Sharon, PA*
- Mercer, PA

  * Ohio counties have not opted-in.

NEW YORK

Albany - Schenectady - Troy, NY
- Albany County
- Greene County
- Montgomery County
- Rensselear County

-       Saratoga County
-       Schenectady County

Jefferson County, NY

Buffalo - Niagara Falls, NY
-       Erie County
-       Niagara County

A proposed rule to remove the above "opt-out" areas from the requirements of the reformulated gasoline program was published June 14, 1995. [On January 1, 1995, a temporary exemption of the RFG requirements in these areas went into effect. On July 1, 1995 this stay was extended until the Agency took final action].

The final rule, published July 8, 1996 [61 FR 35673], formally removed these areas from the list of RFG covered areas and provided states with general opt-out procedures.

The July 8 final rule was superseded by a final rule published October 20, 1997 [62 FR 54552], revising the opt-out procedures.
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ARIZONA

Phoenix nonattainment area
- Maricopa County (partial), AZ

Phoenix opted in the RFG program in 1997; retail stations were required to supply RFG by August 4, 1997.

In September 1997, the Governor of Arizona submitted an RFG opt-out petition for purposes of adopting a more stringent state RFG program in Phoenix.

EPA approved the opt-out petition which became effective on June 10, 1998.

[a/] Source: USEPA, 1998. List of Federal Reformulated Gasoline Program Areas, EPA OMS Reformulated Gasoline, http://www.epa.gov/oms/rfg.htm, USEPA Office of Mobile Sources

[b/] i.e., all ozone nonattainment areas in that state not cited in the "Required Areas" list.

APPENDIX B2

STATE WINTER OXYGENATED FUELS PROGRAMS

Area (C/MSA)	State/ USEPA Region	Control Period/Oxygen Content	Type	Comments
State Winter Oxygenated Fuels Programs[a/] **December 7, 1998**				
New York/ No. N.J./ Connecticut	NY/NJ CONN R2/R1	11/1 -2/29 2.7%	80% to 90% MTBE -- 10% to 20% Ethanol	**OXY & RFG** Will implement for the 98/99 oxy season.
Minneapolis/ St. Paul	MN/R5	Year-Round AVG 3.1% **Approved SIP**	100% Ethanol	Year-round, statewide oxy program.
El Paso	TX/R6	11/1 - 2/29 2.7% **Approved SIP**	100% Ethanol	Maintenance plan continues oxy program. TNRCC has expanded the federal control period to begin Oct. 1 and end on March 31.
Colorado Springs	CO/R8	11/1 to Feb. 7 AVG 3.1% **Approved SIP**	75% Ethanol, 20%TAME & 5%MTBE	Has data to redesignate -- working on redesignation request.
Denver/ Boulder	CO/R8	11/1 to Feb. 7 AVG 3.1% **Approved SIP**	75% Ethanol, 20%TAME & 5%MTBE	**Final redesignation to CO "serious" nonattainment area was published in the FR on 3-10-97 (62 FR 10690-10700).**
Ft. Collins	CO/R8	11/1 to Feb. 7 AVG 3.1% **Approved SIP**	75% Ethanol, 20%TAME & 5%MTBE	Has data to redesignate -- working on redesignation request.
Missoula	MT/R8	11/1 - 2/29 2.7% **Approved SIP**	100% Ethanol	Voluntary ethanol only. Will continue to implement program.
Salt Lake City/Ogden	UT/R8	11/1 - 2/29 **Approved SIP**		This area has never implemented a program. Informal waiver granted. Both areas are developing redesignation requests. SLC will likely remove program from SIP. Ogden has agreed to keep program as contingency measure.
Las Vegas	NV/R9	10/1 - 3/31 3.5%	100% Ethanol	EPA audited in '94 **Final redesignation to CO "serious" nonattainment area was published in the FR on 10-2-97 (62 FR 51604-51606).**

State Winter Oxygenated Fuels Programs[a] December 7, 1998				
Area (C/MSA)	State/ USEPA Region	Control Period/Oxygen Content	Type	Comments
Phoenix	AZ/R9	11/15 - 3/31 3.5%	95% Ethanol & 5% MTBE	EPA audited Dec. '94 **Final redesignation to CO "serious" nonattainment area was published in the FR on 7-29-96 (61 FR 39343-39347).**
Los Angeles*	CA/R9	10/1 - 2/29 1.8% to 2.2%	100% MTBE	**OXY & RFG** **Classified as a "serious" CO nonattainment area.**
Reno	NV/R9	10/1 - 1/31 2.7%	100% Ethanol	EPA audited in Jan. '94. Has data to redesignate -- working on redesignation request.
Grants Pass	OR/R10	11/1 - 2/29 2.7% **Approved SIP**	100% Ethanol	Has data to redesignate -- working on redesignation request.
Klamath Co.	OR/R10	11/1 - 2/29 2.7% **Approved SIP**	100% Ethanol	Has data to redesignate -- working on redesignation request.
Medford	OR/R10	11/1 - 2/29 2.7% **Approved SIP**	100% Ethanol	Has data to redesignate -- working on redesignation request.
Portland	OR/R10	11/1 - 2/29 2.7% **Approved SIP**	100% Ethanol	EPA audited in Feb. '93. Redesignated -- official redesignation date was 10-2-97. Maintenance plan continues program -- area continues to implement program.
Fairbanks	AK/R10	11/1 - 2/29		**Final redesignation to CO "serious" nonattainment area was published in the FR on 2-27-98 (63 FR 9945-9948).**
Spokane	WA/R10	9/1 - 2/29 3.5% **Approved SIP**	100% Ethanol	**Final redesignation to CO "serious" nonattainment area was published in the FR on 3-12-98 (63 FR 12007-12013).**

* CA areas are required to use CA Phase II fuel on June 1, 1996

Oxy Areas Previously Redesignated and No Longer Implementing the Program				
Area (C/MSA)	State	Redesignation Published in FR	Final Redesignation Date	Comments
Syracuse	NY/R2	Sept. 29, 1993	Sept. 29, 1993	
Greensboro	NC/R4	Sept. 21, 1994	Nov. 7, 1994	
Cleveland	OH/R5	Feb. 4, 1994	March 7, 1994	
Duluth	MN/R5	April 14 ,1994	June 13, 1994	
Memphis	TN/R4	July 26, 1994	Sept. 26, 1994	
Baltimore	MD/R3	Oct. 31, 1995	Dec. 15, 1995	
Raleigh-Durham	NC/R4	Aug. 2, 1995	Sept. 18, 1995	
Hartford	CT/R1	May 14, 1995	Jan. 2, 1996	.
Philadelphia	PA/NJ/MD R3/R2	Jan. 30, 1996	March 15, 1996	
Washington	DC/MD/VA R3	Jan. 30, 1996	March 15, 1996	
Albuquerque	NM/R6	June 13, 1996	July 15, 1996	
Vancouver	WA R10	Oct. 21, 1996	Oct. 21, 1996	Redesignation plan drops oxy from the maintenance plan but keeps it as a contingency measure.
Seattle	WA R10	Oct. 11, 1996	Oct. 11, 1996	Redesignation plan drops oxy from the maintenance plan but keeps it as a contingency measure.
Portland	OR/R10	September 2, 1997	October 2, 1997	Redesignation plan keeps oxy program in the maintenance plan
San Diego, Chico, Modesto, Sacramento, Fresno, San Francisco and Stockton, CA	CA/RE 9	March 31, 1998	June 1, 1998	

ORIGINAL AREAS: 39 in 1992, 1 for 1993
36 implemented in first year (1992)

ORIGINAL REQUIRED STATES: 23 Maryland, Massachusetts, North Carolina, Connecticut, Pennsylvania, New Jersey, New York, District of Columbia, Virginia, Ohio, Tennessee, New Mexico, Texas, Colorado, Montana, Utah, Alaska, Oregon, Washington, California, Nevada, Arizona, Minnesota

REDESIGNATIONS: 21 Cleveland, OH; Syracuse, NY; Duluth, MN; Raleigh/ Durham, NC; Winston-Salem-Greensboro, NC; Memphis, TN;
(To date) Baltimore, MD; Washington, D.C., CMSA (VA & MD) Philadelphia, PA CMSA (includes Southern New Jersey); Boston, MA; Hartford, CT; Albuquerque, NM; Vancouver, WA; Seattle, WA; Portland, OR; San Diego, Chico, Modesto, Sacramento, Fresno, San Francisco and Stockton, CA;

PROPOSED OR DEVELOPING: Colorado Springs, CO; Ft. Collins, CO; Grants Pass, OR; Klamath Co., OR; Medford, OR;

REDESIGNATION REQUESTS: 7 Reno, NV; Salt Lake City\Ogden, UT;

OREDESIGNATIONS TO: Denver, CO; Phoenix, AZ; Las Vegas, NV; Spokane,WA; Anchorage & Fairbanks, AK

"SERIOUS" CO NONATTAINMENT AREAS: 6

NOT IMPLEMENTING PROGRAM: Fairbanks, AK; Salt Lake City/Ogden, UT

CURRENT STATES: 14 Connecticut, New Jersey, New York, Texas, Colorado, Montana, Utah, Alaska, Oregon, California, Nevada, Arizona, Minnesota, Washington

TOTAL AREAS IMPLEMENTING IN 1994/95: 31
TOTAL AREAS IMPLEMENTING IN 1995/96: 27
TOTAL AREAS IMPLEMENTING IN 1996/97: 25
TOTAL AREAS IMPLEMENTING IN 1997/98: 25
TOTAL AREAS IMPLEMENTING IN 1998/99: 18

[a/] Source: USEPA, 1998. State Winter Oxygenated Fuels Programs, EPA OMS Fuels Homepage, http://www.epa.gov/oms/fuels.htm#oxy, USEPA Office of Mobile Sources

APPENDIX B3

OXYGENATE TYPE ANALYSIS

Oxygenate Type Analysis 1995 RFG Survey Data
% of Samples with Majority of Oxygen from: *

Survey Area	MTBE	Ethanol	ETBE	TAME	Combo/Other **
Atlantic City, NJ	97.96	1.02	0.00	1.02	0.00
Baltimore, MD	99.74	0.00	0.00	0.26	0.00
Boston-Worcester, MA	95.78	0.30	0.00	3.31	0.60
Chicago-Lake Co., IL, Gary, IN	17.11	82.89	0.00	0.00	0.00
Covington, KY	66.20	32.39	1.41	0.00	0.00
Dallas-Fort Worth, TX	87.17	0.00	2.81	0.00	10.02
Hartford, CT	99.27	0.49	0.00	0.24	0.00
Houston-Galveston, TX	99.56	0.00	0.00	0.22	0.22
Knox Co. and Lincoln Co., ME	100.00	0.00	0.00	0.00	0.00
Louisville, KY	57.71	24.00	17.14	0.00	1.14
Manchester, NH	99.43	0.00	0.00	0.57	0.00
Milwaukee-Racine, WI	16.09	82.59	1.32	0.00	0.00
NY-NJ-Long Is.-CT	98.62	1.38	0.00	0.00	0.00
Norfolk-Virginia Beach, VA	98.68	0.00	0.00	1.32	0.00
Phila.-Wilm, DE-Trenton, NJ	98.45	1.29	0.00	0.26	0.00
Portland, Me	100.00	0.00	0.00	0.00	0.00
Portsmouth-Dover, NH	100.00	0.00	0.00	0.00	0.00
Poughkeepsie, NY	98.96	1.04	0.00	0.00	0.00
Queen Anne Co.-Kent Co., MD	100.00	0.00	0.00	0.00	0.00
Rhode Island	92.73	2.73	0.00	4.55	0.00
Richmond, VA	100.00	0.00	0.00	0.00	0.00
Springfield-MA	96.98	2.11	0.00	0.91	0.00
Sussex County, DE	100.00	0.00	0.00	0.00	0.00
Washington, D.C.-area	99.65	0.35	0.00	0.00	0.00

*RFG Survey samples taken at retail gasoline stations. Categorization based on the oxygenate
  providing more than 50% by weight of total oxygen in a sample.

**The "Other" category is composed of samples containing combinations of oxygenates with
  no single oxygenate providing more than 50% of total oxygen.

Source: USEPA, 1996. Market Share of Oxygenates (PDF), Blue Ribbon Panel
        Homepage, http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm, USEPA office
        of Mobile Sources

Oxygenate Type Analysis 1996 RFG Survey Data
% of Samples with Majority of Oxygen from: *

Survey Area	MTBE	Ethanol	ETBE	TAME	Combo/Other **
Atlantic City, NJ	98.64	0.00	0.00	0.68	0.68
Baltimore, MD	97.42	0.00	0.32	1.94	0.32
Boston-Worcester, MA	95.63	1.31	0.00	3.06	0.00
CT - remainder	99.35	0.65	0.00	0.00	0.00
Chicago-Lake Co., IL, Gary, IN	6.05	93.95	0.00	0.00	0.00
Dallas-Fort Worth, TX	93.89	0.00	0.00	4.20	2.29
Hartford, CT	98.99	1.01	0.00	0.00	0.00
Houston-Galveston, TX	95.00	0.00	0.00	4.06	0.94
Los Angeles, CA	100.00	0.00	0.00	0.00	0.00
Louisville, KY	75.58	24.42	0.00	0.00	0.00
Milwaukee-Racine, WI	3.02	96.64	0.00	0.00	0.34
NY-NJ-Long Is.-CT	99.70	0.30	0.00	0.00	0.00
Norfolk-Virginia Beach, VA	100.00	0.00	0.00	0.00	0.00
Phila.-Wilm, DE-Trenton, NJ	97.99	0.57	0.00	0.57	0.86
Portland, ME	100.00	0.00	0.00	0.00	0.00
Portsmouth-Dover, NH	99.03	0.97	0.00	0.00	0.00
Rhode Island	97.76	1.79	0.00	0.45	0.00
Richmond, VA	100.00	0.00	0.00	0.00	0.00
Sacramento, CA	100.00	0.00	0.00	0.00	0.00
San Diego, CA	100.00	0.00	0.00	0.00	0.00
Springfield-MA	97.79	1.66	0.00	0.00	0.55
Washington, D.C.-area	99.19	0.00	0.00	0.41	0.41

*RFG Survey samples taken at retail gasoline stations. Categorization based on the oxygenate providing more than 50% by weight of total oxygen in a sample.

**The "Other" category is composed of samples containing combinations of oxygenates with no single oxygenate providing more than 50% of total oxygen.

Source: USEPA, 1997. Market Share of Oxygenates (PDF), Blue Ribbon Panel
Homepage, http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm, USEPA office
of Mobile Sources

Oxygenate Type Analysis 1997 RFG Survey Data
% of Samples with Majority of Oxygen from: *

Survey Area	MTBE	Ethanol	ETBE	TAME	Combo/Other **
Atlantic City, NJ	97.47	1.27	0.00	1.27	0.00
Baltimore, MD	98.94	0.00	0.00	1.06	0.00
Boston-Worcester, MA	95.93	1.74	0.00	2.33	0.00
Chicago-Lake Co., IL, Gary, IN	5.84	94.16	0.00	0.00	0.00
Dallas-Fort Worth, TX	100.00	0.00	0.00	0.00	0.00
Hartford, CT	98.44	1.56	0.00	0.00	0.00
Houston-Galveston, TX	92.73	0.00	0.00	6.57	0.69
Los Angeles, CA	100.00	0.00	0.00	0.00	0.00
Louisville, KY	74.75	25.25	0.00	0.00	0.00
Manchester, NH	100.00	0.00	0.00	0.00	0.00
Milwaukee-Racine, WI	4.60	95.40	0.00	0.00	0.00
NY-NJ-Long Is.-CT	98.93	1.07	0.00	0.00	0.00
Norfolk-Virginia Beach, VA	100.00	0.00	0.00	0.00	0.00
Phila.-Wilm, DE-Trenton, NJ	98.69	0.65	0.00	0.98	0.00
Phoenix, AZ	49.18	50.82	0.00	0.00	0.00
Portland, ME	100.00	0.00	0.00	0.00	0.00
Poughkeepsie, NY	97.76	2.24	0.00	0.00	0.00
Rhode Island	98.82	1.18	0.00	0.00	0.00
Richmond, VA	100.00	0.00	0.00	0.00	0.00
Sacramento, CA	100.00	0.00	0.00	0.00	0.00
San Diego, CA	100.00	0.00	0.00	0.00	0.00
Springfield-MA	98.20	1.80	0.00	0.00	0.00
Washington, D.C.-area	98.07	0.00	0.00	1.54	0.39

*RFG Survey samples taken at retail gasoline stations. Categorization based on the oxygenate
 providing more than 50% by weight of total oxygen in a sample.

**The "Other" category is composed of samples containing combinations of oxygenates with
 no single oxygenate providing more than 50% of total oxygen.

Source: USEPA, 1998. Market Share of Oxygenates (PDF), Blue Ribbon Panel
         Homepage, http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm, USEPA office
         of Mobile Sources

1995 RFG SURVEYS Oxygenate Information
Average of Survey Averages

Survey Area	No. of samples	No. of surveys	Average * oxygen wgt. %	Average oxygenate weight percentages *				Percent of total oxygen from each oxygenate *			
				MTBE wgt. %	Ethanol wgt. %	ETBE wgt. %	TAME wgt. %	MTBE O_2 %	Ethanol O_2 %	ETBE O_2 %	TAME O_2 %
Atlantic City, NJ	98	2	2.41	12.59	0.07	0.06	0.28	94.8	1.1	0.4	1.8
Baltimore, MD	392	17	2.20	11.19	0.00	0.11	0.67	92.1	0.0	0.8	4.8
Boston- Worcester, MA	332	4	2.16	10.00	0.02	0.03	1.80	84.1	0.3	0.2	13.1
Chicago- Lake Co., IL, Gary, IN	460	17	2.85	2.05	6.97	0.01	0.02	13.0	85.1	0.0	0.1
Covington, KY	70	2	2.00	7.56	1.58	0.20	0.01	68.5	27.4	1.6	0.1
Dallas- Fort Worth, TX	499	6	2.03	9.16	0.03	0.91	1.01	81.9	0.4	7.1	7.8
Hartford, CT	411	17	2.17	10.50	0.12	0.06	0.99	88.0	1.9	0.5	7.1
Houston- Galveston, TX	468	17	2.09	10.39	0.00	0.02	0.88	90.1	0.0	0.1	6.6
Knox Co. and Lincoln Co., ME	41	2	2.18	11.78	0.00	0.01	0.02	98.0	0.0	0.1	0.1
Louisville, KY	175	2	2.01	5.57	1.49	2.48	0.11	50.3	25.6	19.3	0.9
Manchester, NH	174	4	2.10	10.30	0.00	0.02	1.15	89.2	0.0	0.2	8.6
Milwaukee- Racine, WI	388	17	2.81	2.06	6.65	0.40	0.10	13.3	82.2	2.2	0.5
NY- NJ- Long Is.- CT	434	18	2.37	11.91	0.23	0.06	0.41	91.2	3.3	0.4	2.7
Norfolk- Virginia Beach, VA	151	2	2.05	9.92	0.00	0.36	0.90	87.7	0.0	2.7	6.8
Phila.- Wilm, DE- Trenton, NJ	388	16	2.19	10.95	0.25	0.05	0.34	90.8	3.9	0.4	2.5
Portland, Me	116	2	2.21	11.92	0.00	0.00	0.06	97.7	0.0	0.0	0.4
Portsmouth- Dover, NH	71	2	2.11	10.93	0.00	0.04	0.54	93.8	0.0	0.3	4.0
Poughkeepsie, NY	96	2	2.27	11.89	0.06	0.02	0.26	95.1	1.0	0.1	1.8
Queen Anne Co.- Kent Co., MD	73	2	2.17	10.77	0.00	0.01	0.98	90.0	0.0	0.0	7.1
Rhode Island	110	2	2.25	10.83	0.12	0.01	1.15	87.3	1.9	0.0	8.0
Richmond, VA	137	2	2.14	10.49	0.00	0.02	1.08	88.9	0.0	0.1	7.9
Springfield- MA	331	3	2.15	10.24	0.12	0.05	1.23	86.3	2.0	0.3	8.9
Sussex County, DE	73	2	2.10	9.70	0.00	0.05	1.63	83.7	0.0	0.3	12.1
Washington, D. C.- area	288	4	2.28	11.15	0.02	0.04	1.05	88.9	0.3	0.2	7.2

* e. g. for Atlantic City, NJ the 'average' gallon had 2.41 wgt % oxygen. It is 12.59% MTBE by wgt., therefore about 94.8 % of its oxygen
  comes from MTBE since the oxygen mass fraction in MTBE is 0.1815

Source: USEPA, 1996. Market Share of Oxygenates (PDF), Blue Ribbon Panel

      Homepage, http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm, USEPA office of Mobile Sources

1996 RFG SURVEYS Oxygenate Information
Average of Survey Averages

Survey Area	No. of samples	No. of surveys	Average * oxygen wgt. %	Average oxygenate weight percentages *				Percent of total oxygen from each oxygenate *			
				MTBE wgt. %	Ethanol wgt. %	ETBE wgt. %	TAME wgt. %	MTBE O_2 %	Ethanol O_2 %	ETBE O_2 %	TAME O_2 %
Atlantic City, NJ	147	4	1.89	9.83	0.00	0.02	0.37	94.4	0.0	0.2	3.1
Baltimore, MD	310	12	1.85	8.55	0.00	0.16	1.50	84.0	0.0	1.4	12.7
Boston- Worcester, MA	229	6	2.02	9.54	0.14	0.01	1.32	85.6	2.5	0.1	10.2
CT – remainder	154	5	2.03	10.07	0.07	0.01	0.91	90.1	1.1	0.1	7.0
Chicago- Lake Co., IL, Gary, IN	347	11	3.44	0.60	9.50	0.01	0.00	3.2	96.0	0.0	0.0
Dallas- Fort Worth, TX	262	6	1.88	8.90	0.00	0.03	1.37	85.8	0.0	0.2	11.4
Hartford, CT	298	11	2.05	10.03	0.19	0.02	0.74	88.9	3.2	0.1	5.7
Houston- Galveston, TX	320	12	1.85	8.68	0.00	0.02	1.42	85.2	0.0	0.1	12.1
Los Angeles, CA	90	2	2.05	10.84	0.00	0.00	0.32	95.8	0.1	0.0	2.4
Louisville, KY	258	6	2.01	7.78	1.54	0.02	0.12	70.4	26.7	0.2	0.9
Milwaukee- Racine, WI	298	11	3.14	0.29	8.79	0.05	0.01	1.7	97.0	0.3	0.1
NY- NJ- Long Is.- CT	338	11	2.23	11.57	0.05	0.01	0.43	94.1	0.8	0.1	3.0
Norfolk- Virginia Beach, VA	178	5	1.87	8.81	0.00	0.11	1.35	85.7	0.0	0.9	11.3
Phila.- Wilm, DE- Trenton, NJ	349	12	1.91	9.60	0.06	0.01	0.69	91.0	1.0	0.1	5.6
Portland, ME	134	4	2.10	11.17	0.00	0.03	0.26	96.8	0.0	0.2	1.9
Portsmouth- Dover, NH	103	4	1.99	10.37	0.08	0.00	0.38	94.5	1.3	0.0	3.0
Rhode Island	223	5	2.01	9.77	0.12	0.01	0.95	88.0	2.1	0.1	7.4
Richmond, VA	143	4	1.85	8.68	0.00	0.02	1.45	85.0	0.0	0.1	12.2
Sacramento, CA	88	2	2.11	11.55	0.00	0.00	0.02	99.2	0.0	0.0	0.2
San Diego, CA	86	2	2.02	10.55	0.00	0.00	0.54	94.6	0.0	0.0	4.1
Springfield- MA	181	5	2.05	10.12	0.15	0.00	0.79	89.8	2.6	0.0	6.0
Washington, D. C.- area	246	6	1.90	9.01	0.00	0.05	1.26	86.3	0.0	0.4	10.4

* e. g. for Atlantic City, NJ the 'average' gallon had 1.89 wgt % oxygen. It is 9.83% MTBE by wgt., therefore about 94.4 % of its oxygen comes from MTBE since the oxygen mass fraction in MTBE is 0.1815

Source: USEPA, 1997. Market Share of Oxygenates (PDF), Blue Ribbon Panel

Homepage, http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm, USEPA office of Mobile Sources

1997 RFG SURVEYS Oxygenate Information
Average of Survey Averages

Survey Area	No. of samples	No. of surveys	Average * oxygen wgt. %	Average oxygenate weight percentages *				Percent of total oxygen from each oxygenate *			
				MTBE wgt. %	Ethanol wgt. %	ETBE wgt. %	TAME wgt. %	MTBE O_2 %	Ethanol O_2 %	ETBE O_2 %	TAME O_2 %
Atlantic City, NJ	158	4	2.09	11.02	0.07	0.00	0.3	95.5	1.2	0.0	2.2
Baltimore, MD	282	9	1.94	9.39	0.00	0.00	1.3	88.0	0.0	0.0	10.8
Boston- Worcester, MA	172	4	2.06	9.95	0.05	0.00	1.4	87.8	90.0	0.0	10.4
Chicago- Lake Co., IL, Gary, IN	308	9	3.49	0.57	9.76	0.00	0.0	3.0	97.0	0.0	0.0
Dallas- Fort Worth, TX	260	6	1.96	9.91	0.00	0.00	0.9	91.9	0.0	0.0	7.1
Hartford, CT	256	9	2.09	10.31	0.23	0.00	0.7	89.7	3.8	0.0	5.4
Houston- Galveston, TX	289	9	1.94	9.31	0.00	0.00	1.4	87.2	0.0	0.0	11.1
Los Angeles, CA	178	4	2.04	10.79	0.00	0.04	0.3	96.2	0.0	0.3	2.2
Louisville, KY	198	5	2.23	7.77	2.33	0.00	0.0	63.2	36.3	0.0	0.0
Manchester, NH	114	4	2.01	10.37	0.00	0.00	0.7	93.5	0.0	0.0	5.7
Milwaukee- Racine, WI	239	8	2.97	0.47	8.30	0.00	0.0	2.9	97.1	0.0	0.0
NY- NJ- Long Is.- CT	280	9	2.35	12.14	0.15	0.00	0.4	93.7	2.3	0.0	2.9
Norfolk- Virginia Beach, VA	193	5	1.91	9.47	0.00	0.00	1.1	89.8	0.0	0.0	9.0
Phila.- Wilm, DE- Trenton, NJ	306	9	2.05	10.43	0.06	0.00	0.7	92.2	1.1	0.0	5.6
Phoenix, AZ	183	4	2.73	5.08	5.09	0.00	0.2	33.8	64.8	0.0	1.3
Portland, ME	148	4	2.10	11.37	0.00	0.00	0.2	98.1	0.0	0.0	1.3
Poughkeepsie, NY	134	4	2.24	11.51	0.16	0.00	0.5	93.2	2.5	0.0	3.6
Rhode Island	169	4	1.95	9.71	0.07	0.00	1.0	90.3	1.2	0.0	7.6
Richmond, VA	187	5	1.92	9.17	0.00	0.00	1.5	86.7	0.0	0.0	12.0
Sacramento, CA	166	4	2.03	10.85	0.00	0.00	0.4	96.9	0.0	0.0	2.9
San Diego, CA	170	4	2.09	10.87	0.00	0.06	0.6	94.5	0.0	0.4	4.4
Springfield- MA	167	4	2.06	10.40	0.10	0.00	0.7	91.7	1.7	0.0	5.1
Washington, D. C.- area	259	6	1.96	9.65	0.00	0.00	1.2	89.2	0.0	0.0	9.6

* e. g. for Atlantic City, NJ the 'average' gallon had 2.09 wgt % oxygen. It is 11.02% MTBE by wgt., therefore about 95.5 % of its oxygen
  comes from MTBE since the oxygen mass fraction in MTBE is 0.1815

Source: USEPA, 1998. Market Share of Oxygenates (PDF), Blue Ribbon Panel
        Homepage, http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm, USEPA office of Mobile Sources

APPENDIX B4

SUMMARY OF STATE STANDARDS FOR MTBE

State	Soil Action Level [b]	Soil Cleanup Level [c]	Soil/Drinking Water Level [d]	Groundwater Action Level [b]	Groundwater Cleanup Level [c]	Groundwater/ Drinking Water [e]
Alabama		Risk-based	No		Risk-based	No
Arizona	none established	320 mg/kg[f]-residential 3,300 mg/kg non-residential		none established	none established	none established
Connecticut	>2 mg/kg	2 mg/kg		>100 µg/L[g]	100 µg/L	100 µg/L
Florida	cleanup or monitoring or institutional controls are required whenever cleanup levels are exceeded	350 ppm[h] -direct exposure; 0.2 ppm-leachability		cleanup or monitoring or institutional controls are required whenever cleanup levels are exceeded	35 µg/L	
Idaho	Depends on pathway	Depends on pathway		Depends on pathway	Depends on pathway	52, 261, 511 ppb[i]; depends on use of groundwater
Maryland						50 ppb
Maine	variable depending on proximity of receptors TPH[j] 5 ppm - 10,000 ppm	variable depending on proximity of receptors TPH-5 ppm - 10,000 ppm	50 ppb	25 ppb	25 ppb	50 ppb
Massachusetts	RCS[j]-1 0.3 mg/kg; RCS-2 200 mg/kg	Method 1 Soil-1: GW-1: 0.3 µg/g[k], GW-2: 100 µg/g, GW-3: 100 µg/g Method 1 Soil-2: GW-1: 0.3 µg/g. GW-2: 200 µg/g, GW-3: 200 µg/g Method 1 Soil-3: GW-1: 0.3 µg/g. GW-2: 200 µg/g. GW-3: 200 µg/g		RCGW[l]-1: 0.07 mg/L[n]; RCGW-2: 50 mg/L	Method 1 GW: GW:-1 70 µg/L, GW-2: 50,000 µg/L GW-3: 50,000 µg/L	
Michigan		4,800 µg/L	4,800 µg/L	20 µg/L	240 µg/L	240 µg/L
Missouri	60 ppm if soil is to be used as clean fill	60-280 ppm depending on matrix score		none	400 ppb for nonpotable water; 40 ppb for potable water	none
North Carolina	920 ppb	920 ppb		200 ppb	200 ppb	200 ppb
New Hampshire	2 ppm	2 ppm	NA[o]	70 µg/L	70 µg/L	70 µg/L (advisory)
New Jersey				70 ppb	70 ppb	70 ppb
New Mexico					100 ppb	

TABLE B4.1
SUMMARY OF STATE STANDARDS FOR MTBE[a/]
MTBE TECHNICAL SUMMARY REPORT

State	Soil Action Level [b/]	Soil Cleanup Level [c/]	Soil/Drinking Water Level [d/]	Groundwater Action Level[b/]	Groundwater Cleanup Level [c/]	Groundwater/ Drinking Water[e/]
New York	50 μg/L	50 ppb	50 ppb	50 ppb	50 ppb	50 ppb
Oregon	0.92 - 520 mg/kg	0.92 - 520 mg/kg	0.92 - 2.6 mg/kg	0.18 - 3,000 mg/L	0.18 - 3,000 mg/L	0.18 - 0.51 mg/l
Pennsylvania	NA	0.28 mg/kg	0.28 mg/kg	NA	20 μg/L	20 μg/L
Rhode Island				20 μg/L	40 μg/L	20 μg/L
South Carolina				40 μg/L		
South Dakota	NA	NA	NA	ND[p/]	ND	NA
Utah	>0.3 ppm	0.3 ppm		>0.2 ppm	0.2 ppm	0.07 ppm
Vermont	none established	none established	NA	none established	40 μg/L	40 μg/L
Wisconsin				12 ppb	12 ppb	60 ppb
Wyoming	>cleanup level	313 mg/kg	NA	>0.2 μg/L	0.2 μg/L	0.2 μg/L

[a/] Adapted from Kostecki and Leonard, (1998). Responses were not received from CA or IN. Other states not listed have not yet established standards.

[b/] Action Level: that concentration at which some type of remediation must be undertaken.

[c/] Cleanup Level: that concentration which remediation must achieve.

[d/] States basing soil cleanup levels on concentrations that may leach into drinking water.

[e/] Drinking Water Standard: the level that must not be exceeded in drinking water supplies (primary, seconday, or advisory).

[f/] mg/kg = milligrams per kilogram.

[g/] μg/L = micrograms per liter.

[h/] ppm = parts per million.

[i/] ppb = parts per billion.

[j/] TPH = Total Petroleum Hydrocarbons.

[k/] RCS = Reportable concentration in soil.

[l/] mg/g = micrograms per gram.

[m/] RCGW = reportable concentration in groundwater.

[n/] mg/L = milligrams per liter.

[o/] NA = Not Applicable.

[p/] ND = Not Detectable.

APPENDIX C

**PARTITIONING OF MTBE
BETWEEN
DISSOLVED AND VAPOR PHASES**

APPENDIX C

PARTITIONING OF MTBE BETWEEN
DISSOLVED AND VAPOR PHASES

Partitioning between the dissolved and vapor phases depends on the value of the Henry's Law constant at the ambient temperature (Lyman *et al*., 1990). Because of its low Henry's Law constant, MTBE readily partitions from the atmosphere to precipitation, and the concentration of MTBE in precipitation is directly related to the atmospheric concentration of MTBE. Assuming a constant concentration of MTBE in air, concentrations of MTBE partitioning from the atmosphere to precipitation will increase with lower temperatures, as demonstrated by the following Henry's Law calculation. According to Henry's Law:

$$P_i = K_H \times C_i^{aq} \tag{C-1}$$

where

P_i = partial pressure of species i in vapor phase (Pascals [Pa]),

K_H = Henry's Law constant of species i (Pa-m^3/mol), and

C_i^{aq} = molar concentration of species i in aqueous phase (mol/ m^3).

The ideal gas law states that the partial pressure of species *i* at a given temperature is:

$$Pi = \frac{n_i \times R \times T}{V} \tag{C-2}$$

where

n_i = number of moles of species i in volume V (dimensionless),

R   = ideal gas constant (8.32 Pa-m^3/mol-K), and

T   = ambient absolute temperature (degrees Kelvin [K]).

According to the ideal gas law, the molar volume of an ideal gas at a temperature of 20°C and a pressure of one atmosphere (293K and 100,000 Pa) is:

$$V = \frac{n_i \times R \times T}{P_i} = \frac{1\ mol \times 8.32\ Pa - m^3/mol - K \times 293K}{100{,}000\ Pa} \quad \text{(C-3)}$$

$$V = 0.024\ m^3 \text{ (or about 24.4 liters [L])}.$$

Using the relationship:

$$\mu g/m^3 = \frac{ppb - v \times molecular\ weight}{molar\ volume} \quad \text{(C-4)}$$

a volumetric concentration of 30 ppb-v of MTBE in air at 20°C (293K) corresponds to a mass-based concentration of about 110 µg/m^3, and a molar concentration of about 1.25 x 10^{-6} mol/m^3 in air at 293K. The molar volume of an ideal gas at standard pressure and a temperature of 5°C (278K) is about 23.1 liters; therefore, a volumetric concentration of 30 ppb-v of MTBE in air at 5°C (278K) corresponds to a mass-based concentration of about 114 µg/m^3, and a molar concentration of about 1.29 x 10^{-6} mol/m^3 in air at 278°K.

It is possible to estimate the concentrations of MTBE in precipitation in equilibrium with MTBE vapor in air at a particular temperature (say, 20°C [293K]) by combining Henry's Law (Equation C-1) and the ideal gas law (Equation C-2):

$$C_{MTBE}^{aq} = \frac{P_{MTBE}}{K_H^{MTBE}} = \frac{n_{MTBE} \times R \times T}{K_H^{MTBE} \times V} \quad \text{(C-5)}$$

The molar concentration of MTBE in a unit volume (1 m^3) of air is about 1.25 x 10^{-6} mol at 20°C (293K). This vapor-phase concentration is in equilibrium with some aqueous-phase concentration of MTBE in a unit volume (1 m^3) of water. Substituting a representative value of the Henry's Law constant for MTBE (1 x 10^{-4} atm- m^3/mol; Table 2.1) into Equation C-5 yields:

$$C_{MTBE}^{aq} = \frac{1.25 \times 10^{-6}\ mol \times 8.32\ \dfrac{Pa - m^3}{mol - K} \times 293K}{1 \times 10^{-4}\ \dfrac{atm - m^3}{mol} \times \dfrac{10^5\ Pa}{atm}} \quad \text{(C-6)}$$

$$C_{MTBE}^{aq} = \frac{3.1 \times 10^{-4}\ mol}{m^3} \times \frac{88.15\ g\ MTBE}{mol} \times \frac{1 m^3\ water}{10^6\ g\ water} \times \frac{1{,}000\ g\ water}{L\ water} \quad \text{(C-7)}$$

$$C_{MTBE}^{aq} = 27\ \mu g/L$$

Therefore, an aqueous-phase concentration of about 27 µg/L of MTBE (MTBE in precipitation) is in equilibrium with an atmospheric concentration of 30 ppb-v of MTBE, at a temperature of 293K (20°C).

APPENDIX D

CHEMICAL ANALYSES FOR FUEL CONSTITUENTS IN ENVIRONMENTAL SAMPLES

APPENDIX D

CHEMICAL ANALYSES FOR FUEL CONSTITUENTS IN ENVIRONMENTAL SAMPLES

The variable composition of refined petroleum products has significant implications for their identification and quantitation. Chemical analysis for petroleum hydrocarbon compounds is used throughout site investigation and remediation for several purposes, including:

- To identify and quantitate the constituents present;

- To monitor the progress of remediation as it proceeds; and

- To verify that cleanup goals have been achieved at the conclusion of remediation.

In general, water samples are easier to analyze than soil samples, because water samples are more homogeneous than soil samples. Soils by nature are heterogeneous materials, and their actual inorganic and organic composition can vary dramatically over small distances. Homogeneity is desirable from an analytical standpoint, because a homogeneous sample is more representative of site conditions at a given place and time. Heterogeneous samples are more likely to contain elevated concentrations of chemicals, not typical of site-wide conditions.

Because petroleum products are mixtures of many different chemicals, special problems occur in analyzing for these chemicals, and data interpretation becomes complex (Nyer and Skladany, 1989). Analytical methods for "petroleum hydrocarbons" in environmental samples are "aggregate", in that no effort is made to distinguish among compounds or hydrocarbon classes during analysis. Analytical results are typically expressed in terms of "total fuel hydrocarbons" (TFH), with the label "total" implying that analysis for TFH includes all fuel hydrocarbons. This is far from true. Although several analytical methods are available, each actually measures only a specific range of the constituent hydrocarbons present; analytical results are reported as hydrocarbon concentrations within a specific elution range, comparable to the elution range (hence, hydrocarbon composition), of a particular fuel type. For example, an analytical result, reported as TFH (diesel) indicates only that the hydrocarbons detected in the sample were generally within the molecular range of C-10 through C-24 (typical of diesel fuel). In the absence of instrument calibration against a known standard fuel, a result reported as TFH (diesel) does not necessarily mean that diesel-range fuel hydrocarbons are actually present. Furthermore, because the composition of refined petroleum products varies among sources and through time (as a result of weathering and environmental transport processes), the same concentration of "total fuel hydrocarbons" at different sites may represent very different mixtures, with associated different risks to human health and the environment.

The method most commonly used to analyze for petroleum hydrocarbon compounds in environmental samples is Method 8015 (modified), standardized by the U.S. Environmental Protection Agency (USEPA, 1986a), and adopted by most states, including California (Zemo *et al.*, 1995). Method SW8015 (modified) is a gas chromatographic (GC) analytical method that quantifies the amount of volatile or semi-volatile hydrocarbon compounds that elute within a selected range of boiling temperatures or molecular weights. Because Method SW8015 (modified) is fundamentally an aggregate measurement, it has a number of interpretational difficulties, the most important being that it is non-constituent-specific in nature, and transmits no direct information about which chemicals (alkanes, alkenes, or aromatic hydrocarbons) are present. The analytical results produced using this method thus cannot be used to accurately assess the solubility of the chemicals present, the potential threats to human health and the environment posed by those chemicals, or even the correct type of petroleum fraction in the sample. Furthermore, aggregate analyses for petroleum hydrocarbons (including Method SW8015) are subject to a number of positive interferences, most commonly the incorporation of non-fuel-derived hydrocarbons, such as soluble, oxidized biodegradation products (e.g., alcohols) or biogenic materials (e.g., lipids) into the analytical result. Biodegradation is an important natural process at most sites where petroleum has been released to the environment, and it is reasonable to expect that samples of soil or water from such sites may contain the byproducts of biodegradation. Other difficulties that arise in the interpretation of analytical results for fuel hydrocarbons are associated with the effects of weathering of the fuel in the environment (Zemo *et al.*, 1995). Although Method SW8015 (modified) is useful for assessing the distribution and concentrations of fuel hydrocarbons in a general way, because MTBE cannot be directly identified using the method, its application is not appropriate for situations in which MTBE may be a fuel constituent of interest.

Analyses for particular volatile fuel constituents (in particular, the BTEX compounds) are usually conducted using EPA Methods SW8020A and SW8021B (SW8020A/21B). These analytical methods use purge-and-trap techniques at the method of sample introduction, and gas chromatography (GC) for analyte separation, with analytes identified and quantified by means of a photo-ionization detector (PID). Because PIDs are non-compound-specific detectors, data of high quality can only be obtained if target analytes are completely separated from signal-producing interferences (e.g., other gasoline constituents) in the GC column. Unsaturated compounds containing one or more double bonds can produce strong signal interferences, and high concentrations of saturated hydrocarbons can also cause significant interference. Therefore, false-positive identification or over-estimation of analyte concentrations may occur if analytes and potentially-interfering compounds co-elute (Garrett *et al.*, 1986; Happel et al., 1998).

Method 8260A uses mass spectrometry for analyte detection. Upon bombardment with electrons, organic chemicals disintegrate into unique mass fragments, allowing definitive detection and quantitation of target analytes even if potentially-interfering compounds co-elute with target analytes.

Happel *et al.* (1998) evaluated the ability of current analytical methods to detect fuel oxygenates, including MTBE and TBA, in water samples spiked with gasoline at various concentrations. These investigators found that application of Method SW8020A/21B frequently produced false positive results for all oxygenates tested (i.e., the compounds apparently were detected when they were not, in fact, present). The false-positive

misidentifications resulted from elution of interfering compounds from samples containing elevated concentrations of gasoline constituents. Furthermore, detection limits for Method SW8020A/21B were frequently elevated as a consequence of high concentrations of fuel constituents; and analyses for TBA yielded unreliable results even when gasoline constituents were present in samples at relatively low concentrations (less than 0.5 mg/L). In contrast, Method SW8260A was found to produce excellent results for all oxygenates, regardless of potential gasoline interferences. These results indicate the Method SW8020A/21B is unsuitable for analyses of MTBE and potential degradation daughter products, and should be replaced by Method SW8260A for situations in which MTBE may be a fuel constituent of interest.

Evaluation of MTBE degradation may involve analyses for MTBE daughter products (TBA, TBF) in environmental samples. Concentrations of TBA and TBF in such samples may be extremely low, because the rates of MTBE degradation are generally slow, and the resulting daughter products are not readily detected using conventional techniques. Church *et al*. (1997) propose a new method, using direct aqueous injection onto a polar column, coupled with detection by mass spectrometry (DAI-GC/MS), for analyzing major alkyl ether compounds and their characteristic degradation products at sub-microgram per liter concentrations. Application of the method is summarized as follows.

- Water samples were preserved on ice, and were not acidified, to prevent hydrolysis of TBF.

- Analyte separation for the DAI-GC/MS method was performed by gas chromatography (an HP 5790 instrument) using a 30 m Carbowax stationary phase capillary column (0.25 micrometer EconoCap, or 1.0 micrometer Helifex, both from Alltech).

- Column pressures of 3 pounds per square inch (psi) (for the 0.25 micrometer column) and 8 psi (for the 1.0 micrometer column) were found to be optimal.

- Samples of 10 microliter volume were injected (without additional preparation) into a splitless, 130°C injector, equipped with a 1,000 microliter liner.

- The liner was packed with 1 cm of glass wool, centered 1.5 cm from the bottom. The bottom of the liner protruded 1 cm into the oven.

- The oven temperature was held at 30°C for 3 minutes following sample injection, and was then increased to 220°C, at a rate of 25°C per minute.

- In order to ensure consistent chromatography through many sample injections, water can be removed from the column by baking at 220°C for an additional 10-minute period following a run, or an in-line valve can be used to divert water before it passes onto the column (by switching immediately prior to increasing the temperature).

- A mass spectrometer (Finnigan 4000) was used to detect and identify peaks. Galaxy 2000 software (LGC Sunnyvale, CA) was used for integration of peak areas.

- The mass spectrometer signal was tuned to be optimized in the 35 to 125 *m/z* range for single-ion and multiple-ion detection. Acquisition parameters were set to collect data at the peak center $\pm$ 0.25 *m/z* only.

Detection limits (defined by a 10:1 signal to noise ratio) of 0.1 µG/L were achieved in this study, for MTBE, TBA, and TBF (Church *et al*., 1997).

APPENDIX E

METHODS OF QUANTIFYING BIODEGRADATION RATES

APPENDIX E

METHODS OF QUANTIFYING BIODEGRADATION RATES

Chemical evidence, involving comparison of concentrations of potentially degradable compounds with the concentrations of a conservative tracer can be used to document the occurrence of biodegradation. The following discussion is adapted from the AFCEE Technical Protocol (1995) and other documents (USEPA, 1998d) to address issues specific to consideration of methyl *tert*-butyl ether (MTBE).

E1.0 DATA SET NORMALIZATION

In order to ensure that at least a portion of observed decreases in contaminant concentrations over time can be attributed to biodegradation, measured concentrations of benzene, toluene, ethylbenzene, and xylene isomers (BTEX constituents) or MTBE must be corrected for the effects of dispersion, dilution, and sorption. A convenient way of doing this is to use compounds present in the dissolved plume that are relatively unaffected or predictably affected by biologic or other processes in the subsurface. Measured tracer and contaminant concentrations from a minimum of two points along a flow path can be used to estimate the amount of contaminant that would remain at each point if biodegradation had been the only attenuation process operating to reduce contaminant concentrations. The fraction of contaminant remaining after contaminant removal resulting from all attenuation processes can be computed from the measured contaminant concentrations at two adjacent points. The fraction of contaminant remaining as a result of non-destructive attenuation mechanisms only, can be estimated from the tracer concentrations at the same two points, because an ideal tracer is affected by non-destructive attenuation mechanisms to the same degree as the contaminant of interest and is not affected by biologic processes. The following equation uses these assumptions to solve for the estimated downgradient contaminant concentration if biodegradation had been the only attenuation process operating between two points (*i* and *i*-1) along the flow path:

$$C_{i,corr} = C_{i-1,corr} \left(\frac{C_i}{C_{i-1}} \right) \left(\frac{T_{i-1}}{T_i} \right) \qquad \text{(E-1)}$$

where

$C_{i,corr}$ = corrected contaminant concentration at point i

$C_{i-1,corr}$ = corrected contaminant concentration at point i-1 (if point i-1 is the first or most upgradient point, $C_{i-1,corr}$ is equivalent to the observed contaminant concentration.)

C_I = observed contaminant concentration at point i

C_{i-1} =   observed contaminant concentration at point i-1

T_I =   observed tracer concentration at point i

T_{i-1} =   observed tracer concentration at point i-1

This equation can be used to estimate the theoretical contaminant concentration resulting from biodegradation alone at every point along a flow path on the basis of the measured contaminant concentration at the origin ("source area") and the contaminant/tracer ratios between consecutive points along the flow path. This series of normalized concentrations can then be used to estimate a first-order rate of biodegradation as described in Section E2.0. If, rather than for a series of points, an estimate of the biodegradation rates between only two points (A and B) is desired equation E-1 simplifies to:

$$C_{B,corr} = C_B \left(\frac{T_A}{T_B} \right) \qquad \text{(E-2)}$$

A convenient way of estimating biodegradation rate constants is to use compounds present in the dissolved contaminant plume that that are biologically recalcitrant. One such compound that is useful in some, but not all, groundwater environments is trimethylbenzene (TMB). The three isomers of this compound (*1,2,3*-TMB, *1,2,4*-TMB, and *1,3,5*-TMB) are generally present in fuel mixtures in quantities sufficient to be readily detectable when dissolved in groundwater and are somewhat recalcitrant to biodegradation under anaerobic conditions; however, the TMB isomers do not make good tracers under aerobic conditions (because they are readily biodegraded in aerobic environments). The degree of recalcitrance of TMB is site-specific, and the use of this compound as a conservative tracer must be evaluated on a case-by-case basis. Another compound of potential use as a conservative tracer is tetramethylbenzene; however, detectable dissolved tetramethylbenzene concentrations are generally less common than detectable dissolved TMB concentrations. The apparent recalcitrance and mobility of MTBE in the subsurface suggests that for fuel spills containing MTBE, this compound could itself be used as a tracer during investigations addressing migration and degradation of other (e.g., BTEX) fuel constituents.

An ideal tracer would have Henry's Law and soil sorption coefficients identical to the contaminant of interest, and would thus exhibit similar migration characteristics. However, TMB is more hydrophobic than BTEX or MTBE, resulting in a higher soil sorption coefficient. This causes preferential sorption of TMB, and an increase in the coefficient of retardation for dissolved TMB in the aquifer. Therefore, for these compounds it is advisable to modify equation E-1, to account for the difference in contaminant and tracer velocity resulting from the higher soil sorption and consequent retardation of TMB. Without this modification, using TMB as a tracer can be so conservative that estimated biodegradation rates can be negative.

When the tracer migrates at a velocity that is significantly slower than the compound of interest, it is more important to evaluate contaminant and tracer concentrations after equal travel times rather than equal travel distances, as assumed in equation E-1. The equal time assumption ensures that both the contaminant and tracer are affected to a similar degree by dilution/dispersion and sorption, which are the two dominant non-destructive

attenuation mechanisms in most systems. The ratio of tracer velocity to contaminant velocity can be used to switch from equal travel distances to equal travel times as follows:

$$\frac{V_t}{V_c} = \frac{\left(\dfrac{V_{gw}}{R_t}\right)}{\left(\dfrac{V_{gw}}{R_c}\right)} = \frac{R_c}{R_t} \tag{E-3}$$

where

V_t = *velocity of tracer*

V_c = *velocity of contaminant*

V_{gw} = *velocity of groundwater*

R_t = *coefficient of retardation for the tracer*

R_c = *coefficient of retardation for the contaminant*

The fraction of tracer lost over the time required for the contaminant to travel between points i-1 and i is represented by the expression $R_c/R_t(1-T_i/T_{i-1})$ which is the product of the fraction of tracer lost between travel points and the ratio of retardation factors. Therefore, the fraction of tracer remaining is $1-R_c/R_t(1-T_i/T_{i-1})$. As discussed earlier in this section, the fraction of contaminant remaining after biodegradation is equivalent to the fraction of contaminant remaining as a result of all attenuation processes divided by the fraction of tracer remaining as a result of only non-destructive attenuation processes. Therefore, the corrected concentration at point i can be represented by the following equation:

$$C_{i,corr} = C_{i-1,corr}\left(\frac{C_i}{C_{i-1}}\right)\left(\frac{1}{\left(1-\dfrac{R_c}{R_t}\left(1-\dfrac{T_i}{T_{i-1}}\right)\right)}\right) \tag{E-4}$$

where

$C_{i,corr}$ = corrected contaminant concentration at point i

$C_{i-1,corr}$ = corrected contaminant concentration at point i-1 (if point i-1 is the first or most upgradient point, $C_{i-1,corr}$ is equivalent to the observed contaminant concentration.)

C_I = observed contaminant concentration at point i

C_{i-1} = observed contaminant concentration at point i-1

T_I = observed tracer concentration at point i

T_{i-1} = observed tracer concentration at point i-1

Note: This assumes that $R_t/R_c + T_i/T_{i-1} > 1$.

When R_c is equivalent to R_t, this equation reduces to equation E-1.

E2.0 CALCULATING BIODEGRADATION RATES

Several methods, including first- and second-order approximations, may be used to estimate the rate of biodegradation of organic compounds. Use of the first-order approximation can be appropriate for estimating biodegradation rates for organic compounds in situations where the rate of biodegradation is assumed to be controlled solely by the instantaneous concentration of the contaminant. However, the use of a first-order approximation may not be appropriate when more than one substrate is limiting microbial degradation rates or when microbial mass is increasing or decreasing. In such cases a second- or higher-order approximation may provide a better estimate of biodegradation rates.

E2.1 First-Order Decay

As with a large number of processes, the change in a solute's concentration in groundwater over time often can be described using a first-order rate constant. A first-order approximation, if appropriate, has the advantage of being easy to calculate and simplifying the evaluation of complex phenomenon. In one dimension, first order decay is described by the following ordinary differential equation:

$$\frac{dC}{dt} = kt \qquad (E-5)$$

where
C = concentration at time t $[M/L^3]$
k = overall attenuation rate (first-order rate constant) $[1/T]$

Integrating this differential equation and solving yields:

$$C = C_o e^{-kt} \qquad (E-6)$$

The overall attenuation rate groups all processes acting to reduce contaminant concentrations and includes advection, dispersion, dilution from recharge, sorption, and biodegradation. To determine the fraction of the overall attenuation that can be attributed to biodegradation, these effects must be accounted for, and subtracted from the total attenuation rate. Two methods for determining first-order biodegradation rates at the field scale are presented. The first method involves the use of a normalized data set to compute a decay rate. The second method was derived by Buscheck and Alcantar (1995) and is valid for steady-state plumes. The AFCEE Technical Protocol document (1995) compares the application of these two methods with respect to BTEX biodegradation.

E2.2 Use of a Normalized Data Set

In order to ensure that observed decreases in contaminant concentrations can be attributed to biodegradation, measured contaminant concentrations must be corrected for the effects of advection, dispersion, dilution from recharge, and sorption, as described in Section E1.0 using equation E-1. The corrected concentration of a compound is the

concentration that would be expected at one point (B) located downgradient from another point (A) if the processes of dispersion, dilution from recharge, volatilization, and sorption had not been occurring between points A and B.

The biodegradation rate can be estimated between any two points (A and B) of a normalized data set (where point A is upgradient of point B) by substituting the normalized concentration at point A, $C_{A,corr}$, for C_0, and the normalized concentration at point B, $C_{B,corr}$, for C in equation E-6. The resulting relationship is expressed as:

$$C_{B,corr} = C_{A,corr}e^{-\lambda t}$$
(E-7)

where $C_{B,corr}$ =   normalized contaminant concentration at downgradient point B (from eq. E-2)

          $C_{A,corr}$ =   normalized contaminant concentration at upgradient point A (from eq. E-2). Note that if point A if the first point in the normalized data set, then $C_A = C_{A,corr}$

          λ =   first-order biological decay rate (first-order rate constant) [1/T]

          t   =   time of contaminant travel between points A and B

The rate constant in this equation is no longer the total attenuation rate, k, but is the biological decay rate, λ, because the effects of advection, dispersion, dilution from recharge, and sorption have been removed (Section E1.0). This relationship can be used to calculate the first-order biological decay rate constant between two points by solving equation E-7 for λ:

$$\lambda = -\frac{\ln\left(\dfrac{C_{B,corr}}{C_{A,corr}}\right)}{t}$$
(E-8)

The travel time, t, between two points is given by:

$$t = \frac{x}{v_c}$$
(E-9)

where   x   =   distance between two points [L]

          v_c =   retarded solute velocity [L/T]

The simplest way to calculate the first-order rate constant using an entire set of normalized data is to generate a log-linear plot of normalized contaminant concentrations versus travel time. If the data plot along a straight line, the relationship is first-order and an exponential regression analysis can be performed. The exponential regression analysis produces the equation of the line of best fit for the data being regressed from a log-linear plot and has the general form:

$$y = be^{mx}$$
(E-10)

where   y = y axis value
         b = y intercept
         m = slope of regression line
         x = x-axis value

When using normalized data, x is the downgradient contaminant travel time and m is the biodegradation rate constant, λ. The Pearson product-moment correlation coefficient (R^2), is a measure of how well the regression relationship approximates the data. Values of R^2 can range from 0 to 1; the closer R^2 is to 1, the more accurate the relationship describing the trend in the data. Values of R^2 greater than 0.80 are generally considered good; R^2 values greater than 0.90 are considered excellent. Several commonly available spreadsheets can be used in the exponential regression analysis.

An accurate first-order biological decay rate can be calculated only if biodegradation at a particular site is a first-order process. Normalized contaminant concentrations must first be plotted on log-linear paper to ensure that biodegradation is a first order process.

E2.3 Method of Buscheck and Alcantar (1995)

Buscheck and Alcantar (1995) derive a relationship that allows calculation of first-order decay rate constants for a contaminant in a steady-state plumes. This method involves coupling the regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) to an analytical solution for one-dimensional, steady-state, contaminant transport that includes the effects of advection, dispersion, sorption, and biodegradation. For a steady-state plume, the first-order decay rate is given by (Buscheck and Alcantar, 1995):

$$\lambda = \frac{v_c}{4\alpha_x}\left(\left[1 + 2\alpha_x\left(\frac{k}{v_x}\right)\right]^2 - 1\right) \qquad (E-11)$$

Where: λ = first-order biological decay rate
          v_c = retarded contaminant velocity in the x-direction
          α_x = dispersivity
          k/v_x = slope of line formed by making a log-linear plot of contaminant concentration versus distance downgradient along flow path

The first step in applying the method is to confirm that the contaminant plume has reached a steady-state configuration. This is done by examining historical concentration data to make sure the plume is no longer migrating downgradient and contaminant concentrations are not changing significantly through time. This is generally the case for older spills where the source has not been removed. The next step is to generate a log-linear plot of contaminant concentration versus distance downgradient. Using linear regression, the ratio k/v is first determined. When applying the method of Buscheck and Alcantar (1995), y in the regression analysis (equation E-10) is the contaminant concentration, x is the distance downgradient from point (A), and m is the ratio k/v. The value of k/v determined from the regression analysis is entered into equation E-11 and the biodegradation rate constant, λ, is calculated. Use of two methods to determine first-order decay rate constants at the field scale is a good check on the accuracy of the

calculations. For further discussion, refer to the AFCEE Technical Protocol (1995) or other documents (USEPA, 1998d).

APPENDIX F

**COMMENTS TO DRAFT REPORT
BY
WASTE POLICY INSTITUTE
WITH
PARSONS ES'RESPONSES**

14 September 1999

Mr. Jerry Hansen
Technical Program Manager
AFCEE/ERT
3207 North Road, Bldg. 532
Brooks AFB, TX 78235-5363

Subject: Response to Comments on the Draft Technical Summary Report titled: The
            Fuel Oxygenate Methyl-*Tert*-Butyl Ether (MTBE) – its Movement and Fate in
            the Environment and Potential for Natural Attenuation, February 1999 (AMC
            Contract F11623-94-D0024, RL71)

Dear Mr. Hansen:

   Enclosed please find response to comments on the Draft Technical Summary Report
titled: The Fuel Oxygenate Methyl-*Tert*-Butyl Ether (MTBE) – its Movement and Fate in
the Environment and Potential for Natural Attenuation. This report was prepared by
Parsons Engineering Science, Inc. (Parsons ES) for the Air Force Center for
Environmental Excellence Technology Transfer Division (AFCEE/ERT) and the Air
Mobility Command (AMC).

   The intent of the technical summary report was to determine the potential for natural
attenuation (primarily biodegradation) of MTBE in groundwater. The draft technical
summary report was submitted to AFCEE in February 1999. Comments on the draft
report were received from AFCEE as reviewed by Robert Edwards of the Waste Policy
Institute (WPI), dated 30 March 1999. Responses to these comments were prepared by
Parsons ES and are attached to this letter.

   If you have any questions or require additional information, please call me at (303)
831-8100.

                            Sincerely,

                            PARSONS ENGINEERING SCIENCE, INC.

                            Bruce M. Henry, P.G.
                            Project Manager

Enclosures
c.c. John Anthony – Parsons ES

<div align="center">

RESPONSES TO
WASTE POLICY INSTITUTE COMMENTS ON
THE DRAFT TECHNICAL SUMMARY REPORT TITLED:
THE FUEL OXYGENATE METHYL-TERT-BUTYL ETHER (MTBE) -
ITS MOVEMENT AND FATE IN THE ENVIRONMENT AND POTENTIAL FOR
NATURAL ATTENUATION

</div>

Principal Reviewer: Robert Edwards (210) 321-5136

GENERAL COMMENTS

Comment 1)   Overall, the treatment of fate and transport of MTBE was sufficient to provide an understanding of the physico-chemical behavior of MTBE in the sub-surface environment, especially in relation to petroleum (fuel) hydrocarbon contaminants. But, for this document to be useful to the Air Force, it must provide sufficient information on remediation options for MTBE, Tert-Butyl Formate (TBF), and Tert-Butyl Alcohol (TBA), which it does not. A subsidiary objective of the document would be to assist in the cost-effective remediation of MTBE/TBA/TBF in ground water that may also be contaminated with petroleum fuels. The document is lacking in remediation options for these situations.

Response: *Refer to the objectives of the investigation, and the summary document, as provided in Section 1 (p. 1-2):*

"The objectives of this document are to present an overview of the physical and chemical characteristics of the fuel oxygenate MTBE that influence its movement and fate in the environment, to summarize the literature regarding the results of field-scale and laboratory evaluation of the naturally-occurring breakdown ("degradation") of MTBE, and to provide recommendations for data collection and analysis in support of natural attenuation supplemented with long-term monitoring (LTM) for restoration of groundwater contaminated with MTBE. Specifically, this document is intended to evaluate the biodegradation potential of MTBE, and to describe those conditions under which natural attenuation of MTBE (not necessarily resulting from destructive attenuation processes, including biodegradation) may be a viable remedial option."

As is clear in the above statement of objectives, the scope of work assigned to Parsons ES for this investigation was not to examine the full range of remediation options that could be applied to sites affected by MTBE. Rather, the investigation was specifically intended to examine the literature with regard to evaluating the natural attenuation mechanisms that might act to remove MTBE from the environment, and to provide recommendations regarding the potential for natural attenuation of MTBE and methods for assessing its occurrence. The reality is that MTBE contamination will nearly always co-occur with other fuel constituents and it is unlikely that a remedy selected for MTBE would differ from the remedy(ies) selected for other constituents. For example,

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one would probably not initiate groundwater extraction for MTBE while proposing natural attenuation for benzene, toluene, ethylbenzene, and xylene isomers (BTEX). We therefore feel that this document can serve well as a supplement to existing protocol documents (e.g., AFCEE Technical Protocol, 1995), which also concentrate on aspects of fuel-constituent contamination remedies relying on natural attenuation; and that is how the document was structured.

Comment 2)   Because *in situ* biodegradation is often a feasible remediation option for fuels, this approach would also be an attractive alternative for MTBE if field studies indicated that potential. In fact, a stated objective for the report was "to evaluate the biodegradation potential of MTBE, and describe those conditions under remedial option." To evaluate the feasibility of MTBE biodegradation requires knowledge of the various parameters that contribute to or control the process, such as types of microbes, groundwater pH, dissolved oxygen and other electron acceptors, as well as how they operate to promote biodegradation. This report failed to achieve that objective because results from the field studies were not analyzed to determine the conditions under which biodegradation of MTBE would occur.

Response: *No field data were collected, nor were microcosms constructed or analyzed in conjunction with this investigation. Rather, a principal objective of the investigation, as stated in the Introduction (Page 1-2) was*

". to summarize the literature regarding the results of field-scale and laboratory evaluation of the naturally-occurring breakdown ('degradation') of MTBE .".

Because Parsons ES summarized the results of investigations, as completed and reported by others, we are, of necessity, constrained in our review to reporting only those data and principal conclusions that were generated and previously reported by the original investigators. Providing conclusions regarding the results of investigations completed by others, based on data that may not have been provided or reported, would be, in our view, speculation. In each case-history synopsis we have summarized the relevant conditions under which MTBE degradation did, or did not, occur, as reported by the investigators who completed the study. To assist the reviewer in his evaluation, we have prepared tables, summarizing the conditions reported for each field-scale and microcosm investigation reviewed. Those tables will be provided with the final report.

Comment 3)   In addition to providing insufficient information on conditions under which biodegradation of MTBE prevails, the following generalized comments can be made about the document:

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- It contains too much information of peripheral interest, such as the historical use of MTBE, and the U.S. Environmental Protection Agency's reformulated fuels program. It is suggested that background information be included in an appendix to the document.

Response: *Knowledge of the history of MTBE development and use is relevant to evaluations of petroleum-fuels sites (a primary concern of this document). For example, an investigator assessing a petroleum-spill site at an Air Force facility that ceased active operations in the early- to mid-1980s will probably not be concerned about MTBE based on its history of use in the US. Similarly, an investigator working in areas of the US having a relatively lengthy history of MTBE use may be concerned about non-point source contamination not directly related to a particular site.*

- The document does not adequately present the results of field investigations of MTBE contamination. Each MTBE field investigation case study should be accompanied by at least one diagram of the contaminant plume, preferably overlaid with isopleths for the electron acceptor concentrations. It is recommended that data from the field investigations and the microcosm studies are provided in tabular format. The tables should include at least the following data elements when known: age of plume; estimated percentage of MTBE removed from ground water by natural attenuation processes; estimated biodegradation rate constant of MTBE; analysis (and detection) for tert-butyl alcohol (TBA) and tert-butyl formate (TBF); whether degradation occurred under aerobic or anaerobic conditions; concentrations of electron acceptors in both background and contaminated zones. The goal in providing these data will be to assess prevailing conditions and factors in the sub-surface environment, and attempt generalizations that may be useful at other sites with MTBE contamination.

Response: *Refer to the response to preceding General Comment. In most cases, the requested information (plume" maps, electron-acceptor isopleths) were not provided in the document(s) cited; and in some cases, subsurface conditions (aerobic vs. anaerobic; primary electron acceptors) or occurrence/absence of daughter compounds (e.g., TBA) also were not reported. Where degradation mechanisms, processes, or rates were evaluated by the investigators, these are reported in the case-history summary. Rather than providing the results of investigations, completed by others, at the level of detail requested by the reviewer, a detailed annotated bibliography was provided to assist interested parties in obtaining additional information.*

To assist the reviewer in his evaluation, we have prepared tables summarizing the conditions reported for each field-scale and microcosm investigation

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reviewed in conjunction with this investigation. Those tables will be provided with the final report.

- It is recommended that Appendix C, Biodegradation of MTBE, which discusses the topic in some detail, be incorporated into section 2.7, which discusses the same topic, although not in as much detail.

Response: *The stoichiometry and thermodynamics of the BTEX degradation reactions, provided in Appendix C, refer to degradation mechanisms that have been documented by one or more investigators as actually occurring in field situations. To our knowledge, the actual mechanisms by which MTBE is degraded have not been determined, or documented. The reactions and thermodynamics presented for MTBE in Appendix C therefore represent reactions that are theoretically possible, not reactions that are actually occurring.*

In examining Appendix C, Parsons ES has determined that much of the information provided is probably not germane to the purposes of the current investigation (to present an overview of the physical and chemical characteristics of the fuel oxygenate MTBE that influence its movement and fate in the environment, to summarize the literature regarding the results of field-scale and laboratory evaluation of the naturally-occurring degradation of MTBE, and to provide recommendations for data collection and analysis in support of natural attenuation supplemented with LTM for restoration of groundwater contaminated with MTBE). Accordingly, we will evaluate the material presented in the Appendix, and may include parts of the discussion in the text of the final report, for illustrative purposes only.

- The discussion in Appendix C contains very useful information on the stoichiometric relationships, and thermodynamics, of various metabolic reactions involving MTBE and aromatic (BTEX) compounds. The discussion would prove more useful in evaluating biodegradation of MTBE if it contained information derived from an analysis of field studies, or information on enhancement of MTBE biodegradation.

Response: *Refer to the response to the preceding General Comment.*

- Both hydraulic conductivity and ground-water flow velocity in section 2.7.5 were inconsistently reported with respect to units of measurement. Units used included "ft/day", "meters/day", "ft/year", and "cm/sec". The contractor should select the most appropriate unit for hydraulic conductivity and ground-water

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flow velocity, and convert the data from each case study to those units where necessary.

Response :   *In every case, Parsons ES reported the units as they were presented by original authors. As the site-specific field data were not generated, compiled, or evaluated by Parsons ES, we feel that this is the appropriate procedure. However, for consistency, a conversion to a standard unit (e.g., feet per day [ft/day]) will be added, following expressions in alternate units.*

- The document titled *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* is incorrectly cited throughout the document as Wiedemeier *et al,* 1995. The reference should be changed to "AFCEE *Technical Protocol,* 1995".

Response: *The requested revision will be made.*

- The conclusions and recommendations presented in section 4 did not adequately summarize the limited state of knowledge concerning biodegradation of MTBE and TBA, and did not recommend a course of action to remedy the gaps in the knowledge concerning biodegradation.

Response: *In general, nearly all of the investigators whose studies we examined and cited stated that MTBE degradation was difficult to document at the field scale. We will expand the discussion of recommendations to include specific items (e.g., analyzing for degradation daughter compounds) so that in future, the database for documenting degradation will be larger and more detailed.*

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1	Cover	NA	NA	The title of this document printed on the cover differs from the title printed on the title page. Correct this discrepancy.	This revision will be made.
2	1-1	1	18-22	The last sentence of this page leaves one with the understanding that the concurrent analysis of benzene, toluene, ethylbenzene, xylene isomers, and MTBE can not be achieved. In fact, this document references a method-Direct Aqueous Injection-Gas Chromatography/Mass Spectrometry (DAI-GC/MS)- that readily accomplishes this analysis at very low detection limits. In addition, a GC-Photoionization/Flame Ionization Detection method has been in use for years for the routine analysis of environmental samples containing both BTEX and MTBE. This method is a modification of method SW8020. The sentence should be revised to eliminate the impression that the stated analysis is not available.	The sentence will be revised, as requested.
3	1-5	2	3-6	The statement that a "decrease in contaminant and electron acceptor concentrations can be directly correlated to increases in metabolic byproduct concentrations" implies a false level of precision in performing a mass balance under the typical field conditions. It would be more appropriate to state that the decreases in contaminant and electron acceptor concentrations can be related to increases in metabolic byproduct concentrations.	The comment will be incorporated.
4	2-4	Section 2.2.1	All	Provide a sample calculation for the concentration of MTBE in precipitation derived from this chemical in air. If this type of non-point source is important to the Air Force, more information, such as field studies of the pathway, should be provided.	A sample calculation will be provided. A discrepancy between the calculated value and the value reported in the literature was discovered during calculation and the calculated value (rather than the literature-reported value) will be provided in the text. It is important to be aware of non-point sources of MTBE (and other fuel

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					constituents) in the context of investigation of petroleum fuel contamination, in order to be able to distinguish point-source contamination (spills – the usual object of site investigation) from other potential sources. Non-point source contamination of groundwater could be an important consideration in urban areas, and in particular, at sites located in areas such as described in paragraph 1 (Section 2.2.1). An indication of the magnitude of MTBE concentrations that may be detected in groundwater as a result of non-point sources was presented, and pathways for MTBE to contaminate groundwater (e.g., partitioning of MTBE from air to precipitation) were discussed. The results of a modeling study, which concluded that MTBE can reach groundwater in the cases described, were presented (Page 2-5).
5	2-9	Section 2.4.1.1	2	The boiling point range of gasoline is 40 degrees centigrade (C) to 200 degrees C, not 0 degrees C to 200 degrees C as stated in this section.	Bruya (1993, Table 2) presents a chart showing distillate ranges for a number of refined petroleum products. The boiling-point range presented for gasoline is –0.5°C to 220°C.

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6	2-12	2	3-4	The statement that "all formates contain a doubly-bonded oxygen atom attached to a carbon atom...." is only partly correct, and misleading to the non-chemist. For clarity of presentation it is suggested that the statement be revised to read " formates contain an oxygen atom double-bonded to carbonyl carbon, in addition to another oxygen single-bonded to the carbonyl carbon atom."	The requested change will be incorporated.
7	2-12	2	4-6	The last two sentences of this paragraph should be revised to make the comparisons relative. For example, "the attached oxygen atom imparts a *higher* degree of polarity to this class of compounds", and "As a consequence of their *more* polar molecular structure, ethers, alcohols, and formates tend to be *more* soluble in water *than hydrocarbons containing only carbon and hydrogen* (italicized words are suggested revisions).	Suggested revisions will be incorporated.
8	2-13	First Bullet	1	A pure compound or chemical mixture is not a phase. Revise this bullet to read " In the liquid phase as either a pure compound or a chemical mixture."	The suggested revision will be made.
9	2-13	Second Set of Bullets	All	The chemical properties listed here in bullet form are indeed important elements in understanding the transport and ultimate fate of MTBE, or any other chemical, in ground water. However, the discussion that follows these bullets, including the discussion of transport and attenuation mechanism in Section 2.6, does not clearly explain all of these properties or their effect on fate and transport.	Sections 2.6 and 2.7 combined explain all of the relevant chemical properties and their impact on the fate and transport of MTBE.
				In addition, several of these properties are confusing as listed in these bullets. For example, if the second bullet refers to the vapor pressure, then that should be stated rather than "chemical air-gas diffusion coefficient." Similarly for the third bullet, if the log K_{ow} is intended, that should replace the property given as "chemical water-liquid diffusion coefficient." The last	The terms will be clarified, as appropriate.

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				bullet, given as "rate of chemical decay" is quite misleading since it can be interpreted in several ways	
				Both the bulleted list of properties and the discussion should be revised.	Refer to the responses to Comments Nos. 8 and 9.
10	2-14	1	5-7	The discussion here on subsurface transport references Figure 2.2, but is not clearly depicted in that figure, particularly the location of the capillary fringe. Either revise this text or revise the figure.	The discussion will be expanded, as necessary.
11	2-15	Figure 2.2	NA	This figure depicts a smear zone, but the text does not discuss this important element of the subsurface environment. Also the upper diagram in this figure does not contribute to the text discussion of transport of hydrocarbons, and should be removed to allow expansion of the lower diagram in order to present more detail on the concepts of saturated and unsaturated zones, the capillary fringe, and head pressure.	The discussion will be expanded, and the Figure will be revised, as necessary.
12	2-16	3	5-8	The statement made here concerning the variability of reported values for solubility is generally applicable to values for all chemical properties, not just solubility. This statement should be moved to the introduction of Section 2.6.	The text will be changed to address this concern.
13	2-17	Table 2.1	NA	The inclusion of both ``$K_{oc}$, and "log $K_{oc}$, is redundant. It is recommended that the former be replaced by the commonly used octanol-water partitioning coefficient, ``K_{ow}", in the logarithmic form (i.e., log K_{ow}).	K_{oc} values are more appropriate for evaluating organic carbon partitioning (the underlying process that controls sorption) than K_{ow}. Although reporting K_{oc} and log K_{oc} values may seem redundant, the number is used in both forms in mathematical equations, so the presentation of both values is justified.

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				The last column of this table provides "decay constants" for several organic contaminants in aqueous media. Although these are undoubtedly first order rate constants for microbial degradation, this should be explicitly stated.	The column heading has been clarified as "First-Order Decay Constants".
14	2-19	1	All	The assumption made here that there is no depletion over time of MTBE from a gasoline spill is, of course, unrealistic. MTBE, or any other chemical, will be depleted over time, so that, as the liquid-phase spill ages, the concentration of MTBE will continually decline. As the concentration of MTBE in the liquid phase (gasoline) declines, the amount partitioning into the aqueous phase will also decrease, based on the equilibrium relationship embodied in the partitioning coefficient. Therefore, portions of the ground-water plume nearer to the source (spill) may well exhibit lower concentrations of MTBE than parts of the plume nearer to the leading edge, unless biodegradation has reduced the latter. This section should be expanded to incorporate this concept, which could be useful in interpretation of MTBE analytical results for ground-water samples.	The text will be revised to clarify this point.
15	2-19	3	1-3	The statements made here regarding the solubility of MTBE and its partitioning into the aqueous phase should be relative statements. The wording used here may lead some to conclude that all MTBE in a gasoline spill will instantly and completely partition into the ground water. But based on the K_{ow} of MTBE, at equilibrium more than 90 percent of the MTBE remains in the gasoline phase. Even though the dynamics of the ground water-gasoline interface usually preclude the ideal situation pictured above, the reader should be alerted to the fact that the statements made in the text are relative to the properties of the aliphatic and aromatic hydrocarbon constituents of gasoline.	We concur. The text will be revised to highlight the relative nature of the partitioning.
16	2-20	1	2	The statement that MTBE "is rapidly depleted" should be put into a relative context, and supported by comparative rates of dissolution for it and BTEX	We concur. The text will be revised to highlight the relative nature of the

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				compounds, from one or more field studies.	partitioning. We will examine the literature for comparative rates of dissolution; failing that, we will calculate relative rates of dissolution using Equation 2.6.1 (Page 2-18).
17	2-21	3	3-4	An important point is made in this paragraph, namely that dispersion acts to decrease the concentration of a chemical dissolved in ground water, as distance from the chemical's source area increases. This section should also point out clearly that dispersion acts to increase the volume of contaminated ground water at the same time that it acts to cause concentrations to decrease.	We concur. The text will be revised to note that because no mass removal occurs during dispersion, decreasing contaminant concentrations are equivalent to a larger volume of contaminated water.
18	2-22	2	5	The process of partitioning, quantitatively expressed as the "distribution coefficient", is related to the organic carbon-water partitioning coefficient, "Koc", of a chemical as well as the fraction of organic carbon in the soil. This relationship should be developed more clearly for the benefit of future users of this document not thoroughly grounded in geochemistry and hydrogeology.	The discussion will be expanded.
19	2-23	Table 2.2	NA	To accurately present the range of possible retardation (R3 coefficients and 1/R ratios, the maximum organic carbon fraction (f_{oc}) in Table 3.3 of the AFCEE *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* should be used if an f_{oc}. of 0.02, from Table 3.3 of that document, is used as the maximum value instead of the arbitrarily used 0.001, very different results are obtained. An R value of 2.739, and 1/R value of 0.37, for an f_{oc}, of 0.02 demonstrate that significant retardation of MTBE can occur in soils with high organic carbon content.	The table will be expanded to include a broader range of organic-carbon fractions. However, we note that naturally-occurring organic-carbon fractions greater than about 0.001 – 0.005 are rare in most field soils.
20	2-26	3	1-7	While activation energy is implicitly understood by organic chemists and	The discussion will be expanded to address

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				biochemists, the concept should be illustrated for the reader unfamiliar with it. Including a diagram of a model transition state accompanied by a diagram of energy levels would be helpful in that regard. Secondly, describe how enzyme systems catalyze biological reactions, such as the metabolic utilization of MTBE, by lowering the activation energy of the transition state complex. Microorganisms do not supply the total activation energy required to drive a reaction to completion, and this statement should be deleted in lieu of the enzyme explanation.	these concerns.
21	2-27	2	NA	Accompany this excellent discussion of ground-water reduction-oxidation potential and the hierarchy of electron acceptors with a table or diagram illustrating these.	A figure will be added to illustrate the hierarchy of electron acceptors, and ranges of redox potential.
22	2-30	Figure 2.3	NA	This figure contains a reaction sequence not discussed in the text, namely demethylation to 2-propanol followed by oxidation of the latter to acetone or methyl acetate. Either expand the text discussion to include this facet of the metabolism of MTBE, or make this figure self-explanatory.	The text will be expanded to address the remaining part of the reaction sequence.
23	2-33	4	1-5	The fact that the rate of formation of TBA was experimentally found to be slower than the rate of degradation of MTBE (and rate of formation of TBF) implies a 2-step mechanism (as described) in which TBF accumulation should occur. Discuss any evidence from field or laboratory studies that support or refute this hypothesis.	Steffan *et al.* (1997) and Cowan and Park (1996) report that TBA, and not TBF, was detected as a product of MTBE degradation. Both of these studies measured the rate of TBA degradation and found that TBA degraded more slowly than MTBE. The text in Paragraph 3 has been revised to clarify this point. The MTBE degradation pathway that leads to formation of TBF is reported to be atmospheric photooxidation (Church *et al.*,

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					1997). In Section 2.7.3 we state that accumulation of TBF is not expected because it is readily hydrolyzed to TBA. Figure 2.3 has been modified to clarify the degradation pathway of MTBE. TBF has not been detected in any of the microcosm or field studies discussed in this document. A summary table, documenting the principal features and results of the microcosm studies presented in the text, has been generated, and will be incorporated into this section of the document.
24	2-35	1	All	It is difficult to understand the spatial distribution of electron acceptors without a diagram of their concentrations as well as those of MTBE and its degradation products. What were the background concentrations of the electron acceptors nitrate, sulfate, and ferric (+3) iron?	Reporting the details of the relative depletion or accumulation of geochemical indicator parameters could confuse the interpretation of the mechanism(s) of MTBE biodegradation in this case study. A general description of the pertinent geochemical site conditions is presented in the text. The release of MTBE at this site is a consequence of the release of gasoline containing MTBE. Since the areal "footprints" of the BTEX plume and MTBE plumes are virtually identical the inference that MTBE degradation is occurring because, for example DO is depleted or ferrous iron

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					was detected above background concentrations would be incorrect. The geochemistry at the site indicates primarily that BTEX degradation is occurring. The discussion will be revised to clarify this point.
25	2-36	2	All	It is important for understanding MTBE biodegradation that the reasons for the observation of a 20-day lag period before MTBE degradation started, and cessation of degradation after a reduction of approximately 50 percent of the initial concentration, be understood. Provide a discussion of these observations. Was a quantitative mass balance achieved in this study? If TBF and TBA were analyzed, report the results in this discussion.	The following text will be added to clarify paragraph 2: *"TBA was detected as a product of MTBE degradation. The highest concentration of TBA detected in any microcosm was 0.35 mg/L which occurred immediately after a 0.45 mg/L reduction in MTBE concentration."* Borden *et al*. (1997) provide several possible explanations for cessation of MTBE biodegradation in microcosms. : • Buildup of inhibitory degradation products; • The presence of a minimum degradable concentration; or • Depletion of required nutrients or co-substrates The lag period or acclimation phase has been defined as a change in a microbial

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					community effected by exposure to a chemical resulting in faster biotransformation of that substance (Hickman and Novak, 1989). Possible mechanisms for acclimation include the following: • Enzyme induction, • Mutation or genetic transfer • Growth of the active population(s), • Preferential use of other organic substrates before the compound of interest, • Inactivation or degradation of toxins or inhibitors, and • Limitation of growth rates by nutrient supply or protozoan grazing.
26	2-36	Section 2.5.7.2	NA	This section number is incorrect, as are all of those following this section, up to and including page 2-42. The correct number is Section 2.7.5.2.	The section numbers will be corrected.
27	2-37	3	7	The statement that TBA and TBF "were not observed" is ambiguous. Were the MTBE degradation products TBA and TBF analyzed for and not detected, or were they not analyzed for at all? If the former, then an explanation is needed as to why MTBE concentrations decreased "significantly" but the degradation products were not detected.	The following text will be added to paragraph 2 (first complete paragraph): *"Groundwater samples were analyzed for MTBE and its potential degradation products TBA and TBF. Samples were analyzed at the Oregon Graduate Institute using the direct aqueous injection GC/MS (DAI GC/MS) technique described by Church et al. 1997.*

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					The detection limits for this analysis were 0.1 g/L for MTBE, 0.1 g/L for TBA, and 10 g/L for TBF. Neither TBA nor TBF was The following text will be added to the end of paragraph 2: *"Barker et al. (1998) discuss several possibilities for the apparent absence of MTBE biodegradation products:* • *MTBE was not biodegraded.* • *TBA and TBF may be biodegraded rapidly.* • *Because of the slow biodegradation rate of MTBE, TBA and TBF may be present but at concentrations less than the method detection limit."*
28	2-39	1	All	From the discussion of this field investigation it is difficult to determine whether MTBE was biologically degraded aerobically, under iron reducing conditions, or under even more reducing and anaerobic conditions. It is difficult to distinguish the changes in geochemical parameters associated with BTEX biodegradation from those associated with MTBE biodegradation. Clarify the discussion, perhaps by adding a diagram showing contaminant plumes and the distribution of electron acceptor concentrations.	The fact is that in most case studies examined, it was difficult for the principal investigators to determine whether MTBE was biologically degraded, and/or under what conditions.
29	2-40	3	13	Explain how MTBE could "accumulate" at the distal edge of a plume, especially when it has been described in this document as virtually	A more detailed explanation is presented by Weaver *et al*. (1996), the principal

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				unretarded in ground-water transport.	investigators who originally published this case study. They reported that the gradient becomes less steep in distal parts of the plume; however, this discussion is probably not germane for the purposes of the subject document. The primary point to emphasize in the discussion of this case history is that no clear trend was observed in the total mass of MTBE in the plume, during the sampling period. This is lack of trend in MTBE mass can be compared with the trend results of the mass of BTEX – it was possible to demonstrate that BTEX mass was being removed from the plume. Even though BTEX was continuing to leach into the aquifer from the source area, mass was being depleted more rapidly than it was being added. This point will be clarified in the text.
30	2-41	1	2-5	If the rate of "advance" of MTBE was "approximately the same as the rate of advance of benzene", it is incorrect to state that MTBE was regarded as "being unretarded in ground water". Correct this discrepancy.	This statement generalized the constituent velocities for the entire site. The fact is that the center of mass of the MTBE plume has migrated approximately 1,500 feet farther than the center of mass of the BTEX plume. Rates of migration varied from point-to-point within the plumes as a consequence of varying hydraulic gradients (and groundwater

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					flow velocities). Therefore this statement is technically correct. However, the text is somewhat confusing and will be rewritten to more clearly convey those aspects of this case study that are pertinent to the subject document.
31	2-41	2	3-6	The text states that the estimated mass of MTBE in the aquifer appeared to increase between the first and second sampling rounds. The text goes on to state that this was attributed to complete leaching of MTBE from gasoline in the source area. In the previous paragraph it is suggested that MTBE had completely leached from the gasoline by the time groundwater monitoring began. These two statements appear to contradict one another. Clarify the discussion of this site investigation and resolve any discrepancies.	MTBE had been completely leached from the source area by the time sampling began. This point will be clarified in revised text.
32	3-2	2	First Bullet	Much of the text in this bullet does not describe a characteristic of MTBE that affects its potential for natural attenuation, but reiterates peripheral information. A suggested revision of this bullet reads " Due to its solubility in ground water, and its preferential partitioning from soil organic carbon into ground water (relative to BTEX compounds), an MTBE plume may migrate faster than a BTEX plume. In consequence, MTBE and BTEX plumes may become spatially separated after some period of time."	The suggested revision will be incorporated.
33	3-3	Third Bullet	1-4	As mentioned in an earlier comment, MTBE is "virtually unretarded" in ground water transport only in soils of low organic carbon. Even though its mobility in groundwater will always be greater than that of BTEX compounds, the document should amplify the fact that MTBE can be retarded in transport in some soils.	The text will note that in some cases MTBE retardation can occur.
34	3-3	Fifth	1-4	The analytical method being refined at the Oregon Graduate Institute,	Although referenced at other points in the

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		Bullet		which uses direct aqueous injection and gas chromatography-mass spectrometry, should be referenced here for the analysis of MTBE and its biological degradation products. The method is discussed in Appendix D of this document.	document, the DAI GC/MS method will be noted here, as well.
35	3-4	3	5	The statement in the text is suggesting that a primary focus of MTBE natural attenuation studies be the "distance and time required for dispersion," or dilution of the MTBE concentration to below a regulatory threshold. Conceptually, this may be a valid approach if a completed exposure pathway is absent. In reality it is unlikely that regulators will permit contaminant dilution in ground water as a sole remedy. The focus of a natural attenuation evaluation should be the feasibility of biodegradation. Change this text.	We concur that <u>one</u> of the focuses of a natural attenuation evaluation should be the feasibility of biodegradation. However, USEPA and other regulatory agencies specifically acknowledge the existence of other natural-attenuation mechanisms (including dispersion). The USEPA (USEPA, 1998) defines natural attenuation as: *"Naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in these media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization, and chemical or biological stabilization or destruction of contaminants."* The text will be revised, as necessary, to clarify this point.
36	3-9	First Bullet	9-12	The possibility for hydrolysis of an aliphatic ether bond in aqueous solution is rather remote, especially at low temperature. Concentrated mineral acid at elevated temperature is required to effect this cleavage. However, acidification as a sample preservation measure should be avoided because of the deleterious effect of the mineral acid on the carbowax phase of the gas	The discussion will be modified to incorporate this information.

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				chromatography column. The text should be modified in accordance with this chemical information.	
37	3-13	2	3-8	To make this a "stand-alone" document, it is necessary to include more information, including sample calculations, on the correction of observed concentrations of contaminants, using procedures previously developed for petroleum hydrocarbon biodegradation studies. The procedure using recalcitrant hydrocarbons, such as the tetra-methyl benzene isomers, as tracers to correct for physical attenuation of contaminant concentrations should be included in this section.	The referenced calculational technique is used to "normalize" the concentrations of a constituent of concern (e.g., BTEX), to the concentrations of a relatively mobile, and recalcitrant, compound (used as a tracer) to estimate ranges of degradation rates. In fact, MTBE is perhaps the most mobile, and most recalcitrant, constituent currently found in petroleum fuels, and could be used as a tracer in place of the less mobile tri- and tetramethylbenzenes. Application of this procedure, using MTBE, will be discussed.
38	3-17	3	13-19	See comment number 35 concerning physical attenuation of contaminant concentrations versus evaluation of biodegradation, and make the necessary changes to this section.	We disagree. While we acknowledge the importance of destructive attenuation mechanisms, it is necessary for practicing professionals and the regulatory community to understand that the other attenuation mechanisms can be protective of human health and the environment. Accordingly, the text will not be revised.

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39	4-1	3	2	Complete the sentence.	The sentence will be completed as follows: *"The following significant observations, conclusions, and recommendations are derived from the existing body of technical literature regarding the properties, occurrence, movement, and fate of MTBE in the environment."*
40	4-2	Fifth Bullet	1-3	This statement again describes MTBE as virtually unretarded during ground-water transport, without specifying the organic carbon content of the soil. Make the necessary changes to the text as previously described for this topic.	In most circumstances, MTBE <u>is</u> virtually unretarded – an organic carbon content of 0.02 is, in most geologic settings, unrealistically high. Furthermore, a geologic material having an organic carbon content of 0.02 will almost certainly also have a high clay content, so that the more significant factor in transport then becomes, not retardation, but hydraulic conductivity (resulting in low groundwater flow velocity). However, the text will be revised to indicate that retardation may occur in some circumstances.
41	4-3	Fifth Bullet	1-3	MTBE degradation is not necessarily difficult to document at the field level as stated here. Rather, it appears from the discussion of field studies included in this report that at least some of those studies did not thoroughly attempt to document all of the necessary parameters, or did not use analytical methods with the required sensitivity and accuracy. Only when MTBE degradation is documented at the field level will the regulatory community accept bioremediation as a tool for use in appropriate situations. The text should be modified as indicated here, or deleted altogether.	In general, nearly all of the investigators whose studies we examined and cited stated that MTBE degradation was difficult to document at the field scale. We will expand the discussion of recommendations to include specific features (e.g., analyzing for degradation daughter compounds) so that in future, the database for documenting

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					degradation will be larger and more detailed.
42	C-3	1	16-17	As previously discussed, microorganisms do not provide activation energy. Rather, they provide enzyme systems that lower activation energy in the transition state, and thus facilitate biochemical reactions. Change the text accordingly.	The text will be revised to clarify this point.
43	C-4	Table C-2	18-19	Correct the character spacing in the chemical reactions in these lines.	Formatting issues will be addressed in the final document.
44	C-9	Table C-3	7	The last chemical equation on this page, for MTBE oxidation coupled with methanogenesis, is incorrectly balanced. Correct the stoichiometry and verify that the G° value has been correctly calculated. In addition, the chemical formula for MTBE is missing an oxygen atom in the first, second, third, fourth, and sixth chemical equations.	The reaction stoichiometry will be corrected.
45	C-10	2	11-14	It may be worthwhile to add to this discussion of microbial metabolism of MTBE that the recalcitrance of this compound, in spite of favorable thermodynamics, is no doubt due to the presence of the sterically bulky tert-butyl group. The latter sterically blocks access to the carbon-oxygen bond, thus slowing or preventing degradation of the molecule. This leads to a higher transition state activation energy, requiring an enzyme to facilitate reaction at the ether bond. The acclimation of a microbial consortium mentioned here may involve the growth of a distinct microbial population containing an enzyme system capable of catalyzing reactions of MTBE or ethers in general.	A discussion to this effect will be added to the text. The reviewer is requested to recommend references that can be used as citations, to supplement the text.
46	C-13	2	All	The relevance of this paragraph to the overall discussion of aerobic metabolism is unclear. Either expand or modify the text to flow with the rest of the section, or remove it entirely.	The text will be modified to clarify the discussion.

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47	C-14	Table C-4	Row 3	The value of 0.34 for the mass of MTBE degraded aerobically per unit mass of electron acceptor differs from the value in Table C-3. Correct the discrepancy	The discrepancy will be corrected.
48	C-14	3	1-7	This discussion of oxygen requirements and stoichiometric relationships is somewhat confusing. The discussion implies that the stoichiometry' of the reaction of MTBE with an electron acceptor (oxygen) will change due to variable microbial energy requirements. Of course, the basic stoichiometry remains the same as regards MTBE oxidation, even though total oxygen usage by microorganisms may vary with growth rates and cell maintenance requirements. Clarify this discussion.	The discussion will be clarified.