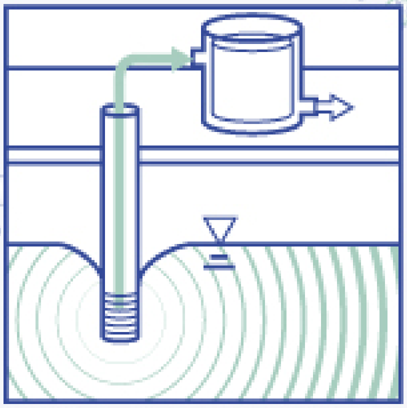
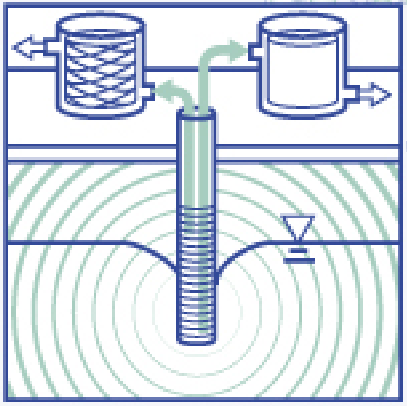
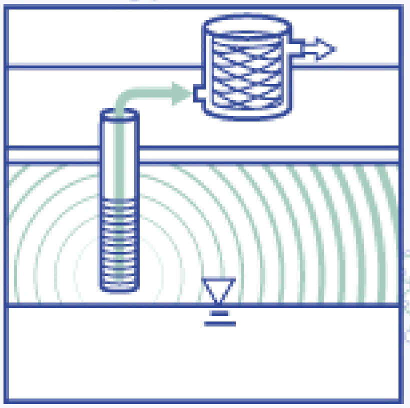
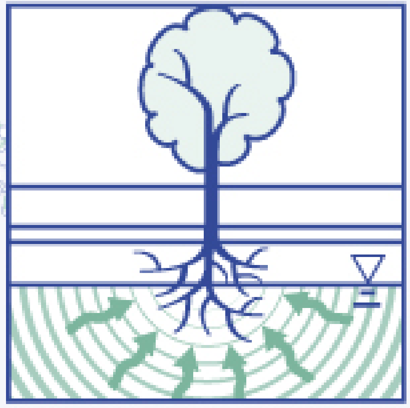
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

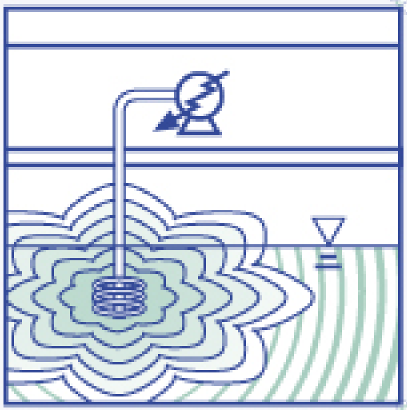
Technologies For Treating MtBE and Other Fuel Oxygenates

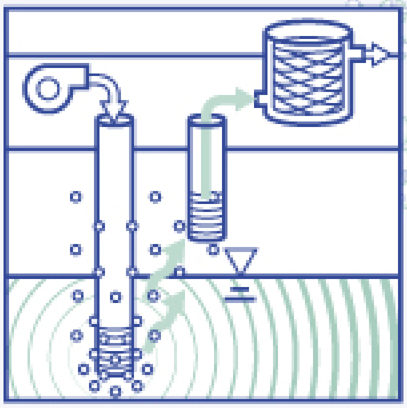


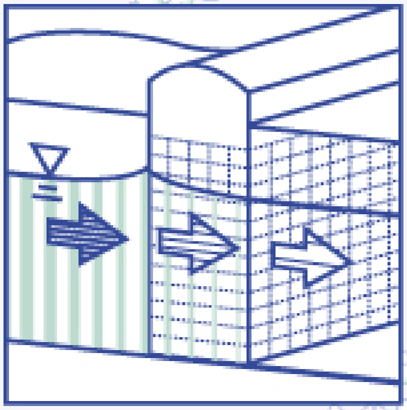


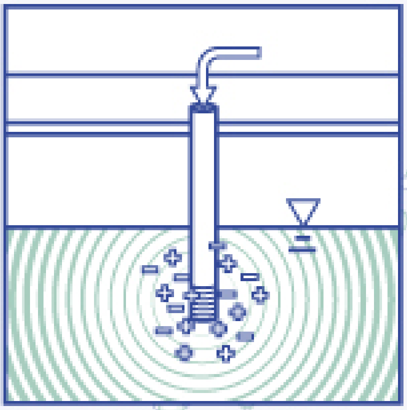


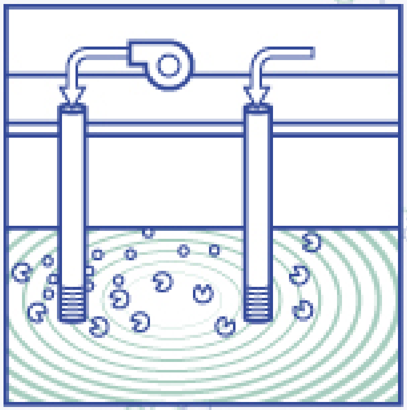












May 2004

Technologies for Treating MtBE and Other Fuel Oxygenates

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Office of Superfund Remediation and Technology Innovation
Washington, DC 20460

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LIST OF ACRONYMS AND ABBREVIATIONS

AST	Aboveground storage tank
bgs	Below ground surface
BTEX	Benzene, toluene, ethylbenzene, and xylenes
cfm	Cubic feet per minute
ClO_2^-	Chlorine dioxide
CLU-IN	EPA's Hazardous Waste CLeanUp INformation System
CO_2	Carbon dioxide
COD	Chemical oxygen demand
cy	Cubic yard
DIPE	Diisopropyl ether
DL	Detection limit
DPE	Dual-phase extraction
EPA	United States Environmental Protection Agency
EtBE	Ethyl tert-butyl ether
FRTR	Federal Remediation Technologies Roundtable
Ft	Feet/foot
GAC	Granular activated carbon
gals	Gallons
gpm	Gallons per minute
H_2O_2	Hydrogen peroxide
HP	Horse power
IC	Institutional controls
K	Hydraulic conductivity
LNAPL	Light non-aqueous phase liquid
lbs	Pounds
MC	Mixed culture
MCL	Maximum Contaminant Level
mg/L	Milligrams per liter
MNA	Monitored natural attenuation
MnO_4	Permanganate
mm Hg	Millimeters of mercury
MPE	Multi-phase extraction
MtBE	Methyl tert-butyl ether
NAPL	Non-aqueous phase liquid
ND	Non detect
NEIWPCC	New England Interstate Water Pollution Control Commission
NO_3^-	Nitrate
NOM	Natural organic matter
NSCEP	National Service Center for Environmental Publications
O_3	Ozone
OCl^-	Hypochlorite
O&M	Operation and maintenance
Oxyfuel	Oxygenated fuel
ppmv	Parts per million by volume
PRB	Permeable reactive barrier
psi	Pounds per square inch
PVC	Polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
RFG	Reformulated gasoline
RO	Reverse osmosis
ROI	Radius of influence
S_2O_8	Persulfate
SC	Single culture
scfm	Standard cubic feet per minute
SERDP	Strategic Environmental Research and Development Program
SO_4^{-2}	Sulfate
SSTL	Site specific target level
SVE	Soil vapor extraction
TAA	Tert-amyl alcohol
TAEE	Tert-amyl ethyl ether
TAME	Tert-amyl methyl ether
TBA	Tert-butyl alcohol
TBF	Tert-butyl formate
TPE	Two-phase extraction
TSP	Trisodium phosphate dodecahydrate
USACE	United States Army Corps of Engineers
UST	Underground storage tank
UV	Ultraviolet
VE/GE	Vapor extraction/groundwater extraction
VOC	Volatile organic compound
µg/kg	Microgram per kilogram
µg/L	Microgram per liter
µm	Micrometer
ZOI	Zone of influence

FOREWORD

Fuel oxygenates, including methyl tert-butyl ether (MtBE), have been widely used in the United States for the past several decades as an additive to gasoline intended to either boost octane ratings or to reduce air pollution. The gasoline containing these oxygenates has been stored in aboveground and underground storage tanks at a wide range of facilities, including refineries, terminals, service stations, and by end users; and gasoline has been transported throughout the U.S. via pipeline, barge, rail, and truck. As a result of leaks and spills, MtBE, other fuel oxygenates, and other gasoline components have been found in soil and groundwater at these sites. Federal and state studies have found that these components, including MtBE, have reached drinking water sources in many locations, including areas where the use of oxygenated fuel has not been mandated.

The U.S. Environmental Protection Agency (EPA) has identified several hundred MtBE-contaminated sites that have performed treatment of soil and groundwater to remove or destroy MtBE. Many of these sites have also treated other fuel components, primarily benzene, toluene, ethylbenzene, and xylene (BTEX), and some have treated fuel oxygenates other than MtBE. Although others have reported about treatment technologies for MtBE cleanup, only limited information has been published about cleanup of other oxygenates. These oxygenates include ether compounds, such as ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), diisopropyl ether (DIPE), and tert-amyl ethyl ether (TAEE), as well as alcohol compounds, such as tert-butyl alcohol (TBA), tert-amyl alcohol (TAA), ethanol, and methanol.

This report provides an overview of the treatment technologies used to remediate groundwater, soil, and drinking water contaminated with MtBE and other fuel oxygenates. The treatment methods discussed include air sparging, soil vapor extraction, multi-phase extraction, *in situ* and *ex situ* bioremediation, *in situ* chemical oxidation, pump-and-treat, and drinking water treatment. Information in the report can be used to help evaluate those technologies based on their effectiveness at specific sites. The report summarizes available performance and cost information for these technologies, examples of where each has been used, and additional sources of information.

This report may be useful to cleanup professionals and researchers; federal, state, and local regulators; remediation consultants; water treatment plant designers and operators; and other interested parties. The report is intended to be a screening tool that can be used to identify treatment technologies for soil, groundwater, and drinking water contaminated with MtBE and other fuel oxygenates. However, it should be considered only as a starting point for such an analysis. The applicability of a particular treatment technology is site specific, and depends heavily on factors such as site conditions and treatment goals. Decisions about the use of a specific treatment approach will require further analysis, possibly including treatability or pilot-scale studies. This report is not a guidance document and is not intended to prescribe specific treatment technologies for certain types of applications. It was written assuming that readers have a basic technical understanding of the treatment technologies and the chemistry discussed.

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A PDF version of this report is available for viewing or downloading from the Hazardous Waste Cleanup Information (CLU-IN) system web site at http://www.cluin.org/mtbe. Printed copies of the report can also be ordered through that web address, subject to availability. For more information regarding this report, contact Linda Fiedler, EPA Office of Superfund Remediation and Technology Innovation, at (703) 603-7194 or fiedler.linda@epa.gov.

ACKNOWLEDGMENT

Special acknowledgment is given to the federal and state staff and other remediation professionals for providing information for this document. Their cooperation and willingness to share their expertise about treatment technologies used to address MtBE and other oxygenates encourages their application at other sites.

1.0 INTRODUCTION

1.1 What is the Purpose of This Report?

This report provides an overview of treatment technologies used to remediate groundwater, soil, and drinking water contaminated with methyl tert-butyl ether (MtBE) and other fuel oxygenates. The purpose of this report is to:

- Identify technologies used to treat MtBE and other fuel oxygenates
- Help screen those technologies based on their effectiveness in treating particular media and contaminants under specific site conditions and application requirements
- Provide available performance and cost information about the use of those technologies
- Provide additional information relevant to the treatment of MtBE and other fuel oxygenates
- Identify additional sources of information

This report is intended to be a screening tool that can be used to identify treatment technologies for groundwater, soil, and drinking water contaminated with MtBE and other fuel oxygenates. However, it should be considered only as a starting point for such an analysis. The applicability of a particular treatment technology is site specific and depends heavily on factors such as site conditions and treatment goals. Decisions about the use of a specific treatment technology will require further analysis, possibly including treatability studies.

The performance and cost data in the report can help cleanup professionals, site managers, remediation consultants, and others gain a broader understanding of the types of technologies that have been used to treat MtBE and other fuel oxygenates, as well as the types of information available from sites that have used those technologies. This report also provides information about the factors that potentially affect the performance and cost of those technologies.

This report is not a guidance document and is not intended to prescribe specific treatment technologies for certain types of applications. It was written assuming that readers have a basic technical understanding of the treatment technologies and chemistry discussed. Readers requiring additional background information on the treatment of MtBE and other oxygenates are referred to the information sources listed in Section 6.0.

1.2 Who is the Intended Audience of This Report?

The information presented in this report may be useful to cleanup professionals and researchers; federal (Superfund and Resource Conservation and Recovery Act (RCRA) remediation site managers), state, and local regulators; remediation consultants; water treatment plant designers and operators; and other interested parties.

1.3 What Information Sources Were Used to Prepare This Report?

The sources of information used to prepare this report include EPA's MtBE Treatment Profiles Website, located at http://www.cluin.org/products/mtbe, technical publications, and other industry sources. As discussed below and summarized in the text box on the following page, EPA's treatment profiles website presents information about drinking water and remediation sites that treat soil and groundwater for MtBE. Additional information sources used to prepare this report included EPA reports, other technical publications, recent conference proceedings (such as from the National Ground Water Association and

Battelle conferences), and contacts knowledgeable about projects involving remediation of MtBE, including project managers and vendors. A list of these sources is included at the end of this report, with specific sources cited throughout the body of the report. A complete summary of the project data included in this report is contained in Appendix A. EPA has provided a contaminant focus area for MtBE at www.cluin.org/mtbe.

EPA's MtBE Treatment Profiles Website

EPA's MtBE Treatment Profiles Website, available at www.cluin.org/products/mtbe, provides site-specific data about the use of *in situ* and *ex situ* technologies that have been used to treat MtBE in groundwater, soil, and drinking water. Profiles contain the following types of information, as available: project information, such as site background and setting, contaminants and media treated, and area of contamination and quantity treated; technology design and operation; cost and performance information, including cleanup goals; points of contacts; and references. Profiles are available for nearly one dozen types of technologies, and are updated/expanded several times a year. The profiles are based on information provided by site managers, regulatory officials, and technology providers, as well as from published reports and conference proceedings. The website can be searched using pick lists for selected parameters or by using a list of all available profiles. Each profile has a varying level of detail, depending on the data and information that was available.

As of January 2003, the website contained information about 323 projects, including information about the technology used, project scale, performance, and cost. Twenty-nine of these projects reported data on other fuel oxygenates, including tert-butyl alcohol (TBA) for all 29 projects, tert-amyl methyl ether (TAME) for 3 projects, ethanol for 3 projects, and diisopropyl ether (DIPE) for 1 project. This report discusses information available as of January 2003; however, it should be noted that the web site since has been expanded to include information about additional projects; as of April 2004, the web site included a total of 390 projects. A summary of information about the 390 projects was presented at the National Ground Water Association conference on MtBE and Perchlorate, June 4, 2004, in a paper titled "Application and Performance of Technologies for Treatment of MtBE and Other Oxygenates", available at www.cluin.org/mtbe.

The performance and cost data included in this report are primarily based on the database of information from 323 site cleanups (projects) that involved treatment of MtBE and other fuel oxygenates. No additional testing of technologies was performed during the preparation of this report, and no independent review was performed for the data in the database. Generally, the available information included information about technology design and operation, such as number and types of wells, additives, and flow rates, as well as use of multiple technologies for a given project. In addition, project scale (full, pilot, bench) and status (completed or ongoing) were typically identified. In some cases, only interim data for ongoing projects are available.

1.4 Considerations About the Performance and Cost Data Included in This Report

The treatment performance and cost data presented in this report provide users with:

- Data from actual field applications, focusing on full-scale and relatively large field demonstrations, including design and operation information about use of treatment technologies at more than 300 projects
- Information about both conventional and innovative technologies that have been used to successfully treat MtBE
- Preliminary information about treatment of fuel oxygenates other than MtBE

- Lessons learned about the application of these technologies to cleanup media contaminated with MtBE and other fuel oxygenates

The performance and cost data presented in this report are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website. There was variation among the profiles in the level of detail for performance and cost data by project. Many of the treatment profiles contained only limited information about treatment performance and cost, generally including a maximum concentration of MtBE for before-treatment and a maximum concentration after-treatment. These concentrations often were limited to discussing how the treatment technology performed relative to the cleanup goals for the site. Most treatment profiles did not provide detailed performance data, such as MtBE concentration versus time over the duration of the project, or statistical evaluations of performance data with confidence limits.

Treatment performance and cost are site specific and depend on many factors. These factors include site conditions (such as soil types, permeability, conductivity, redox conditions, and degree of heterogeneity), technology design and operation, and regulatory considerations such as cleanup levels. Additional factors include duration of the release (such as a gasoline leak), presence of down-gradient water supply wells, and distribution of contaminants in soil and groundwater.

While EPA has not promulgated a federal cleanup level for MtBE, some states have established cleanup levels. However, as shown in Table 2-1, these vary by state, ranging from 5 to 202,000 µg/L, a difference of more than three orders of magnitude. Because of the variation in MtBE cleanup levels, after-treatment MtBE concentrations are reported based on information provided in the source documents, and are not compared against a common cleanup level for all projects.

Projects generally reported concentrations of MtBE in groundwater or drinking water, with only limited projects reporting MtBE concentrations in soil. As such, the technology performance information in this report is presented primarily in terms of changes in concentration of MtBE in water. Performance data are shown as the highest concentration reported prior to beginning treatment and the highest concentration after treatment was completed (shown as “final concentration”). For projects that are ongoing, the final concentration shown is the most current concentration reported in the source document. Final concentrations identified in source documents as below a reported detection limit (DL), but which do not provide a DL, are shown in this report as non-detect (ND).

For projects where more than one technology was used, such as a site that used air sparging, *in situ* chemical oxidation, and SVE, performance information is presented under each of the technologies used for that project.

With regard to treatment cost data, this report provides a summary of available data based on information in the source materials. These cost data are intended to give a broad indication of the types of costs associated with cleanup projects, and users should be cautious about drawing conclusions about the cost of cleanup projects at specific sites based on these data. As discussed in more detail later in the report, very few projects provided sufficient information to calculate a unit cost for treatment.

In addition, cost data are presented in terms of the total cost for cleaning up contaminated sites. In some cases, the specific components that make up the total cost were not provided in the source materials, such as for capital or operation and maintenance (O&M) activities. In other cases, the types of contaminants present at the sites, other than MtBE, were not identified in the source materials. Sites may have been contaminated with gasoline components such as petroleum hydrocarbons, as well as oxygenates, and the treatment costs reported could be for cleanup of gasoline components as well as the oxygenates. For example, for a specific project, most of the cost for cleanup may be due to gasoline components other than oxygenates.

EPA recently prepared a more detailed analysis of treatment cost for *in situ* treatment of fuel oxygenates. The paper, “Cost of *In Situ* Treatment of Fuel Oxygenates”, was presented at the National Ground Water Association conference on Remediation: Site Closure and the Total Cost of Cleanup, New Orleans, held November 13-14, 2003, and is available at www.cluin.org/mtbe.

1.5 Report Organization

The remainder of this report provides a summary of the information available about the treatment of MtBE and other fuel oxygenates at the 323 projects reviewed and from other industry sources. Chapter 2 provides background information about fuel oxygenates, including information about their properties. Chapter 3 provides a comparison of the treatment technologies used to treat oxygenates, while Chapter 4 includes technology-specific discussions for technologies used to treat soil, groundwater, and drinking water. Chapter 5 provides information about non-treatment remedies. Chapter 6 contains a list of the references used to prepare this report. A complete summary of the project data included in this report is contained in Appendix A, available through www.cluin.org/mtbe. This appendix is organized by treatment technology and contains a summary of key information for each project.

2.0 BACKGROUND

2.1 What are Fuel Oxygenates?

Fuel oxygenates are oxygen-containing compounds used as gasoline additives to increase octane ratings and produce cleaner burning fuel. The common oxygenates fall into two major chemical groups – ether compounds, consisting of organic compounds characterized by an oxygen atom linking two hydrocarbon groups; or alcohols, consisting of an alkyl group (such as methyl, ethyl, or isopropyl) bonded to a hydroxyl (oxygen-hydrogen) group. In addition to MtBE and ethanol, other common oxygenates include TBA, TAME, ethyl tert-butyl ether (EtBE), and DIPE. Tert-amyl ethyl ether (TAEE), tert-amyl alcohol (TAA), and methanol have also been used to a lesser extent. Figure 2-1 shows the molecular structure of commonly-used oxygenates. Some of these oxygenates could also be present in commercial formulations of other oxygenates as by-products or degradation products. For example, TBA is often found in commercial formulations of MtBE.

Oxygenates came into widespread use in the U.S. in the late 1970s as an octane booster, replacing alkyl lead additives, which were being phased out in an effort to reduce lead emissions from vehicles. The use of oxygenates in gasoline was increased after the passage of the 1990 Clean Air Act Amendments that included requirements to increase the oxygen content of fuel to reduce air emissions. The amendments required the use of oxygenated fuel (Oxyfuel) with a minimum of 2.7 percent by weight oxygen in 39 carbon monoxide non-attainment areas during wintertime and Reformulated Gasoline (RFG) with a minimum of 2.0 percent by weight during the remainder of the year (Blue Ribbon Panel on Oxygenates in Gasoline, 1999).

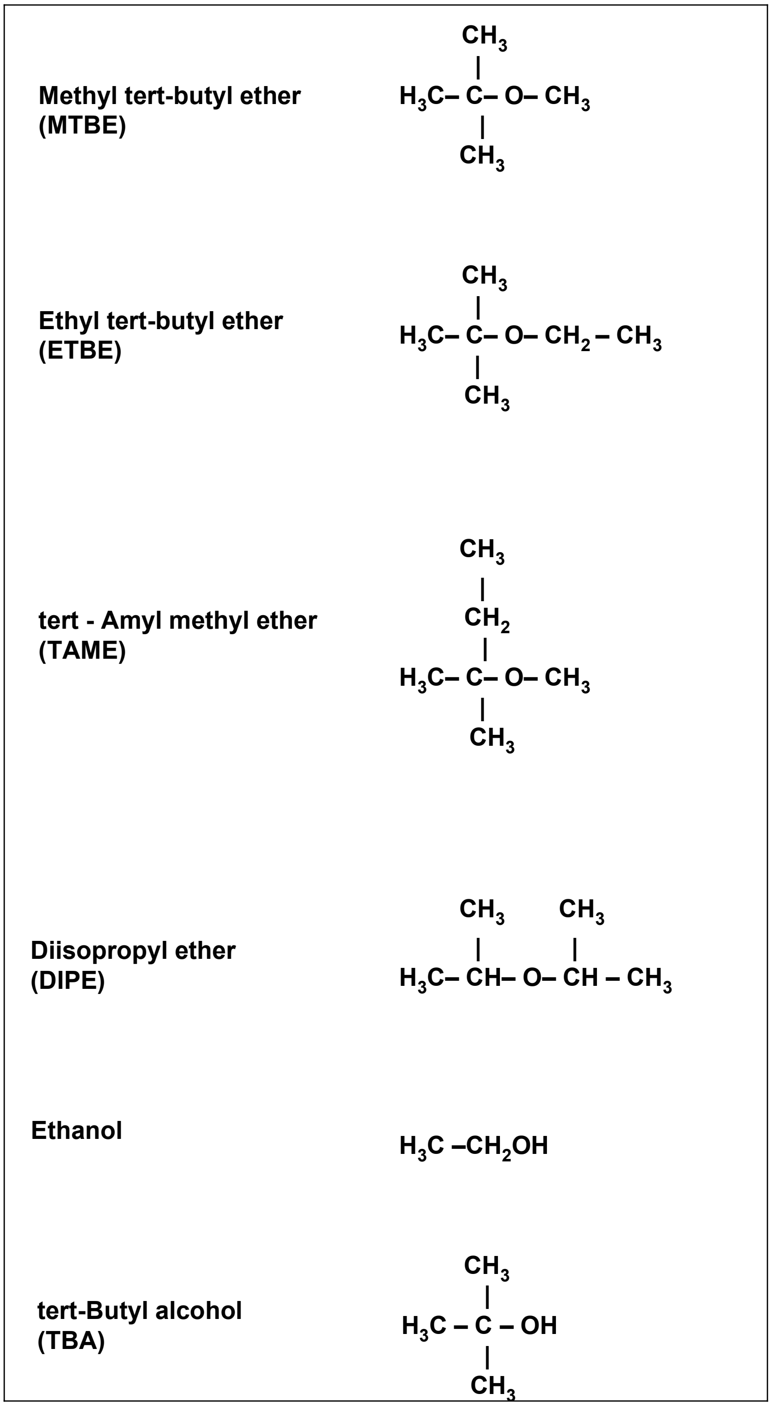
In 1998, approximately 30 percent of all gasoline in the U.S. contained oxygenates. At that time, MtBE was the most common fuel oxygenate, present in more than 80 percent of oxygenated fuels. However, due to increasing restrictions on the use of MtBE, this percentage has decreased over the past several years. In 1998, ethanol was the second most common fuel oxygenate, present in about 15 percent of oxygenated fuels. Other oxygenates were used in the remaining 5 percent of oxygenated fuels. As of 2002, 17 states and the District of Columbia were required to use gasoline that contains MtBE or other oxygenates to reduce air pollution. Recent surveys have found that MtBE is present in states that did and did not use RFG. MtBE has been found in gasoline, as well as heating oil and diesel fuel. Sources of MtBE included areas used for storage, transportation, and use (McGarry, 2002).

The following documents contain additional information on the historic use of oxygenates:

- Blue Ribbon Panel on Oxygenates in Gasoline. 1999. Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline. EPA 420-R-99-021. http://www.epa.gov/oms/consumer/fuels/oxypanel/blueribb.htm

- EPA. 1998. MtBE Fact Sheet #3: Use and Distribution of MtBE and Ethanol. EPA Office of Underground Storage Tanks. EPA 625-K-98-001. September. http://www.epa.gov/swerust1/mtbe/mtbefs3.pdf

Figure 2-1. Molecular Structures of Common Fuel Oxygenates



Methyl tert-butyl ether (MTBE)

$H_3C-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-O-CH_3$

Ethyl tert-butyl ether (ETBE)

$H_3C-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-O-CH_2-CH_3$

tert - Amyl methyl ether (TAME)

$H_3C-\overset{\substack{CH_3\\|\\CH_2\\|}}{\underset{\substack{|\\CH_3}}{C}}-O-CH_3$

Diisopropyl ether (DIPE)

$H_3C-\overset{\substack{CH_3\\|}}{CH}-O-\overset{\substack{CH_3\\|}}{CH}-CH_3$

Ethanol

H_3C-CH_2OH

tert-Butyl alcohol (TBA)

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

2.2 What Are the Sources of Oxygenates in the Environment?

As discussed above, oxygenates have been widely used in the U.S. for the past several decades as an additive to gasoline intended to either boost octane ratings or to reduce air pollution. A significant proportion of the more than 100 billion gallons of gasoline used in the U.S. annually has contained MtBE and other oxygenates at greater than 10 percent by volume. The volume of MtBE, ethanol, and other oxygenates used in RFG and Oxyfuel in 1997 was estimated to be about 11 million, 2 million, and 700,000 gallons, respectively (White et al, 2002). The gasoline containing these oxygenates is stored in aboveground storage tanks (ASTs) and underground storage tanks (USTs) at a wide range of facilities, including refineries, terminals, service stations, and by end users; gasoline has been transported throughout the U.S. via pipeline, barge, rail, and truck. There are an estimated 3.7 million USTs in the U.S., including 700,000 regulated gasoline USTs at approximately 250,000 facilities and approximately 3 million underground fuel storage tanks that are exempt from federal regulations (for example, certain farm and residential and home heating oil tanks) (Blue Ribbon Panel Report, 1999). Gasoline has been released to the environment through spills and leaks from ASTs and USTs, as well as from manufacturing, storage, and transport operations.

2.3 What is the Prevalence of Contamination by Oxygenates in the Environment?

MtBE has been detected nationwide in soil and groundwater. Federal and state studies have found that MtBE contamination has reached drinking water sources in many locations, including areas where the use of oxygenated fuel has not been mandated (GAO, 2002). This MtBE contamination has also been documented in surface water bodies resulting from direct spills, storm water runoff, and emissions from watercraft. The following federal and state studies contain additional information on the extent of contamination by MtBE:

- GAO. 2002. Testimony Before the Subcommittee on Environment and Hazardous Materials, Committee on Energy and Commerce, House of Representatives, Environmental Protection, MtBE Contamination from Underground Storage Tanks, Statement of John Stephenson, Director, Natural Resources and Environment. GAO.02.753T. May 21. http://www.gao.gov/

- New England Interstate Water Pollution Control Commission (NEIWPCC). 2003. A Survey of State Experience with MtBE Contamination at LUST Sites. August. http://www.neiwpcc.org/mtbesum.pdf

- Lawrence Livermore National Laboratory. 1998. An Evaluation of MtBE Impacts to California Groundwater Resources. UCRL-AR-130897. July 11. http://www-erd.llnl.gov/mtbe/pdf/mtbe.pdf

- Maryland Department of the Environment. 2001. The Task Force on the Environmental Effects of MtBE. Final Report. December. http://www.mdarchives.state.md.us/msa/mdmanual/26excom/defunct/html/23mtbe.html

Of the 44 states that reported testing for MtBE at leaking tank sites, 35 states reported finding MtBE in the groundwater at least 20 percent of the time they sampled for it. Twenty four states reported finding MtBE at least 60 percent of the time (GAO, 2002).

Information about the prevalence of other oxygenates in the environment is limited. However, there is evidence that other oxygenates may be found at sites contaminated with MtBE; non-MtBE oxygenates were identified as a contaminant at 29 of the projects in the database. In addition, several surveys, including those identified below, have assessed the nature and extent of contamination with other oxygenates within the U.S.

- U.S. Geological Survey. 2003. A National Assessment of Volatile Organic Compounds (VOCs) in Water Resources of the U.S. Summer 2003. http://sd.water.usgs.gov/nawqa/vocns/

- American Water Works Research Foundation. 2003. Occurrence of MtBE and VOCs in Drinking Water Sources of the U.S. http://www.awwarf.org

- New England Interstate Water Pollution Control Commission (NEIWPCC). 2003. A Survey of State Experience with MtBE Contamination at LUST Sites. August. http://www.neiwpcc.org/mtbesum.pdf

2.4 What are the Concerns About Contamination with Oxygenates?

There have been several assessments of research concerning the health effects of MtBE and other oxygenated fuels (National Science and Technology Council, 1997; California EPA, 1999). Recently, results from research were published about a study of the movement of MtBE between tissues in human volunteers (Prah, 2004). EPA is currently updating its assessment of the health effects of MtBE.

There is uncertainty as to what levels of MtBE in drinking water cause a risk to public health (GAO, 2002). EPA has issued an advisory suggesting that drinking water should not contain MtBE in concentrations greater than 20 to 40 micrograms per liter (µg/L), based on taste and odor concerns, but has not issued a federal maximum contaminant level (MCL) for MtBE, which will be based on the ongoing EPA studies.

In addition, 31 states have established standards, guidelines, advisory levels, or action levels (some based on the EPA advisory concentrations) for the maximum concentration of MtBE allowable in drinking water. Forty two states have established cleanup levels or guidelines (some site-specific) for MtBE in soil and groundwater, as shown at http://www.epa.gov/oust/mtbe/index.htm. MtBE drinking water standards range from 5 to 240 µg/L, with 90 percent of state standards less than or equal to 100 µg/L. Soil cleanup levels range from 5 to 280,000 µg/kg and groundwater cleanup levels range from 5 to 202,000 µg/L, considering both potable and non-potable uses for groundwater (EPA, 2003a; Delta Environmental Consultants, 2004; NEIWPCC, 2000). More than 75 percent of the states have groundwater cleanup values less than 100 µg/L. Delta Environmental Consultants http://www.deltaenv.com/ compiled the summary of state groundwater standards for EPA, and periodically updates their summary of the standards.

Only limited information is available about the health risks of oxygenates other than MtBE. Fewer states have established standards and cleanup levels for these contaminants than for MtBE. Currently, there are no federal drinking water advisory or cleanup levels for these other fuel oxygenates. Several states have established, and some states have plans to establish, cleanup levels for other oxygenates (Delta Environmental Consultants, Inc., 2004). Table 2-1 summarizes the number of states that have cleanup levels for fuel oxygenates along with the range of cleanup levels established for each.

Table 2-1. State Cleanup Levels for Fuel Oxygenates in Groundwater

Fuel Oxygenate	States with Cleanup Level (in 4/04)	Lowest Cleanup Level (µg/L)	Highest Cleanup Level (µg/L)
MtBE	42	13	202,000
TBA	11	12	11,000
DIPE	7	0.438	20,000
TAME	6	25	980
ETBE	5	24	50
Ethanol	6	50	1,900,000
Methanol	11	50	16,000

Note: Cleanup levels address both potable and non-potable sources of groundwater
Source: Delta Environmental Consultants, Inc., 2004

2.5 How Are Oxygenates Assessed in the Environment?

Analytical methods for petroleum hydrocarbons (usually benzene, toluene, ethylbenzene, and xylenes – collectively BTEX) are well established and some of these protocols have been modified to include oxygenates as individual target compounds. Until recently, validated EPA analytical methods existed for only a few fuel oxygenates (specifically ethanol, methanol, and TBA). Methods that were developed for analysis of petroleum hydrocarbons in water samples may not be appropriate for fuel oxygenates for several reasons, such as analytical instruments may not routinely be calibrated for oxygenates, inappropriate methods may be used for sample analysis, detection limits (particularly for alcohols) may be higher than regulatory standards, or acid-catalyzed hydrolysis (breakdown) of ethers may occur during sample processing and analysis. In April 2003, EPA published a Fact Sheet (EPA, 2003a) that specifies the following steps that may be taken to address potential analytical problems with oxygenate analysis. EPA has found that using this approach consistently results in detection limits of 5 µg/L or lower for MtBE, TBA, ETBE, TAME, TAEE, TAA, DIPE, and acetone.

- Routinely calibrate analytical methods for the suite of common fuel oxygenates
- Use Method 8260 (GC/MS) or Method 8015 (GC/FID) for sample analysis
- Modify sample preparation methods to increase sensitivity and decrease detection limits; in some cases, samples should be heated during the preparative phase, especially when analyzing for alcohols
- Change the chemical preservation method to avoid the potential for ether hydrolysis; for example, using base preservation to raise the pH to greater than 11 (including use of trisodium phosphate dodecahydrate [TSP]), rather than acidification, would help avoid ether hydrolysis

Other researchers have provided additional information related to the methods used for the analysis for fuel oxygenates. The following references provide more detailed information about this subject:

- White H., Lesnik B., Wilson J. 2002. Analytical Methods for Oxygenates. L.U.S.T.Line, Bulletin 42, New England Interstate Water Pollution Control Commission. pp 1-8. October. Discusses results from an EPA study to determine optimum conditions for purge-and-trap sample preparation for MTBE and other fuel oxygenates. http://www.epa.gov/oust/mtbe/LL42Analytical.pdf

- Crumbling D.M., Lesnik B. 2000. Analytical Issues for MtBE and Related Oxygenate Compounds. L.U.S.T.Line, Bulletin 36, New England Interstate Water Pollution Control Commission. pp 16-18. Discusses relative appropriateness of using flame ionization detection and mass spectrometry with proper preparation techniques. http://www.epa.gov/oust/mtbe/LL36Methods.pdf

- Halden, R. U., A. M. Happel, and S. R. Schoen. 2001. Evaluation of Standard Methods for the Analysis of Methyl *tert*-Butyl Ether and Related Oxygenates in Gasoline-Contaminated Groundwater. *Environmental Science & Technology*, Vol. 35, no. 7, pp.1469-1474. (Additions and Corrections, Vol. 35, no. 7, p.1560.) Presents results from a formal method evaluation, round-robin study, and a split-sample study (424 groundwater samples) that showed consistently good results for mass spectrometry and flame ionization detection, but not for photoionization detection. http://pubs.acs.org/

2.6 How Do Oxygenates Migrate in the Environment?

MtBE and other oxygenates typically enter the environment blended with gasoline or other refined fuel products. However, these oxygenates migrate differently within the environment because of the differences in physical properties between oxygenates and the other components of gasoline, such as BTEX, of which benzene is typically the most common contaminant of concern. Table 2-2 contains a summary of some properties that influence the migration of MtBE and other oxygenates in the environment. As discussed later in this report, these physical properties also influence the treatability of MtBE and other oxygenates.

Fuel oxygenates generally exhibit the following physical properties relative to benzene:

- Greater tendency to partition into the vapor phase from the non-aqueous phase (vapor pressure) (with the exception of TBA, ethanol, and TAME)
- Greater solubility in water
- Lesser tendency to partition to organic matter in soil (soil adsorption coefficient)
- Lesser retardation factor (slowing of migration with groundwater due to sorption to aquifer matrix)
- Lesser tendency to partition into the vapor phase from the aqueous phase (Henry's Law Constant)

Because of their relatively higher vapor pressure, ether-based oxygenates in fuel will tend to volatilize from releases (non-aqueous phase) exposed to the open air more rapidly than benzene. Alcohol-based oxygenates will volatilize less rapidly than benzene. However, once fuel oxygenates enter the subsurface and become dissolved in groundwater (aqueous phase), they are significantly less volatile (lower Henry's Constant) than benzene. Oxygenates are many times more soluble than benzene; concentrations of MtBE in groundwater as high as 1,000,000 µg/L are not uncommon. Also, because MtBE dissolved in groundwater will partition (as a function of its soil adsorption coefficient) to the organic matter in surrounding soil less readily than benzene, a dissolved MtBE plume typically migrates faster than a dissolved benzene plume (lower retardation factor). As a result, MtBE contamination can result in a relatively larger groundwater plume, compared with plumes originating from gasoline constituents (EPA, 2001a; Kinner, 2001).

While all fuel oxygenates are more water soluble than other gasoline components (benzene), variations in molecular structures result in a range of physical properties and affect the way that each of them migrate in the environment. Figure 2-2 summarizes the physical properties discussed above for each of the common fuel oxygenates relative to benzene, which is most often the chemical of concern in gasoline. While the physical properties for each oxygenate is different, there are similarities among the alcohols and the ethers. For example, as shown on Figure 2-3, alcohol-based oxygenates have a relatively greater water solubility and much lower Henry's Constant than the ether-based oxygenates. Other properties such as the soil partition coefficient, vapor pressure, and retardation factor do not adhere to these same groupings.

2.7 How Do the Properties of Oxygenates Affect Treatment?

As discussed above, the properties of MtBE and other oxygenates, including water solubility, vapor pressure, soil adsorption coefficient, retardation factor, and Henry's Law Constant, affect their fate and transport in the environment relative to other contaminants. These same properties also affect the selection and design of remediation technologies used to address soil and water contaminated with oxygenates. In general, the same types of treatment technologies have been applied for treatment of BTEX and MtBE, however design and operating conditions for MtBE may not be the same as for treatment of BTEX. For example, carbon-based adsorption materials that work well for BTEX may not be effective for removal of MtBE.

BTEX is most often the contaminant group targeted for treatment at gasoline spill sites, and in many cases the treatment systems have been specifically designed to reduce concentrations of benzene. In some cases, a treatment system designed to remove benzene can also remove the oxygenate contamination. However, because of the differences in the physical properties of oxygenates relative to benzene, certain oxygenates might not be effectively treated by a system designed to treat benzene. Also, because the physical properties of individual oxygenates also differ from one another, a treatment system designed to treat one oxygenate may not effectively treat another oxygenate. An overview of the effects of the physical properties of oxygenates on the effectiveness of various remediation technologies is included in Section 4. Primary considerations related to the treatment of oxygenates include:

- The vapor pressures of most oxygenates, with the exception of ethanol, TBA, and TAME, can result in them being more readily volatilized from soil using certain technologies, such as soil vapor extraction (SVE) or multi-phase extraction (MPE) (EPA, 2001b; Kinner, 2001).

- The relatively low Henry's Constants (the ratio of a compound's concentration in air relative to its concentration in water) of oxygenates can result in them being more difficult to strip from contaminated groundwater via air sparging or air stripping as part of a pump-and-treat remedy.

- The presence of an ether bond or hydroxyl group in oxygenates results in these compounds being significantly less likely to partition to organic matter (K_{oc}), such as in use of granular activated carbon (GAC) in pump-and-treat remedies.

- Because they can be chemically oxidized or biologically degraded, chemical oxidation and biodegradation technologies (both *in situ* and *ex situ*) can be effective in the treatment of oxygenates.

Table 2-2. Properties of Fuel Oxygenates and Other Fuel Constituents

Chemical	Pure Phase Solubility (mg/L)	Solubility into H_2O from Gasoline (mg/L)[a]	Log K_{oc}	Vapor Pressure @25ºC (1) @20ºC (2) (mm Hg)	Henry's Law Constant (Dimensionless)	Retardation Factor		Molecular Weight (g/mol)	Boiling Point (EC)	Density (g/L)	Octane Number	Taste Threshold in Water (mg/L)	Odor Threshold (ppm)
						Soil Condition A (4)	Soil Condition B (5)						
Benzene	1,780 (1)	<100 (2)	1.5-2.2 (1)	76-95.2 (1) 73 (2)	0.22 (1)	1.59 (8)	3.38 (8)	78.11 (1)	80.1 (1)	0.88 (2)	94 (2)	500 (2)	0.5 (2)
MtBE	43,000-54,300 (1), 48,000 (2)	5500 (2) 3393 (6) 5241 (7)	1.0-1.1 (1)	245-256 (1) 240 (2)	0.024-0.12 (1) **0.018** @20ºC	1.09 (8)	1.38 (8)	88.2 (1)	55.2 (1)	0.74 (2)	110 (2)	20-40 (2)	0.053 (2)
TBA	Miscible (1), (2)	25,000 (2)	1.57 (1)	40-42 (1) 41 (2)	0.00048-0.00059 (1) **0.00048**	1.31 (8)	2.25 (8)	74.1 (1)	82.4 (1)	0.79 (2)	100 (2)	NA	21 (2)
DIPE	2,039-*9,000 @ 20ºC* (1)	804 (6) 745 (7)	1.46-1.82 (1)	149-151 @ 20ºC (1)	0.195-0.41 (1)	1.37 (8)	2.47 (8)	102.2 (1)	68 (1)	0.73 (3)	NA	NA	NA
ETBE	26,000 (1) 12,000 (2)	3300 (2) 1018 (6) 1365 (7)	1.0-2.2 (1)	152 (1) 130 (2)	0.11 (1)	1.33 (8)	2.34 (8)	102.2 (1)	72.2 (2)	0.74 (2)	112 (2)	47 (2)	0.013 (2)
TAME	20,000 (1) 12,000 (2)	2400 (2) 1210 (6) 1220 (7)	1.3-2.2 (1)	68.3 (1) 75 (2)	0.052 (1)	1.47 (8)	2.89 (8)	102.2 (1)	86.3 (1)	0.77 (2)	105 (2)	128 (2)	0.027 (2)
Ethanol	Miscible (1), (2)	57,000 (2)	0.20-1.21 (1)	49-56.5 (1) 44 (2)	0.00021-0.00026 (1)	1.04 (8)	1.17 (8)	46.1 (1)	78.5 (1)	0.79 (2)	115 (2)	NA	49 (2)
Methanol	Miscible (1)	NA	0.44-0.92 (1)	121.6 (1)	0.00011 (1)	1.04 (8)	1.16 (8)	32.1 (1)	64.7 (1)	0.79 (3)	NA	NA	NA

Notes:

NA - Information not available

[a] "Solubility into H_2O from Gasoline" data from the sources listed below are based on experimental results and estimates for typical gasoline blends in contact with water; actual solubility into water from gasoline is dependent on the fraction of individual gasoline components and, therefore, may vary from the values presented in this table

(1) Data from Zogorski et. al. "Fuel Oxygenates and Water Quality". In Interagency Assessment of Oxygenated Fuels. NSTC. 1997. Data for MtBE for temp = 25 ºC, unless otherwise stated. Additional information about affect of temperature on Henry's Law constant in A. Fischer et. al. "Determination of Henry's Law Constant for MtBE at Groundwater Temperatures", Chemosphere 54 (2004) 689-694.

(2) Data from "Achieving Clean Air and Clean Water: The Report of the Blue Ribbon Panel on Oxygenates in Gasoline," September 1999

(3) Data from NIOSH Pocket Guide to Chemical Hazards (1990)

(4) Soil Condition A: organic fraction $f_{oc} = 0.001$ mg/mg, bulk density = 1.75 kg/L, porosity = 0.25

(5) Soil Condition B: $f_{oc} = 0.004$ mg/mg, bulk density = 1.75 kg/L. porosity = 0.25

(6) Experimental results, ManTech Environmental Research (USEPA Contract 68-C-09-198)

(7) Theoretical results, ManTech Environmental Research (USEPA Contract 68-C-09-198)

(8) Data from "Guidelines for Investigation and Cleanup of MtBE and Other Ether-Based Oxygenates," CalEPA, State Water Resources Control Board, March 2000

Figure 2-2. Physical Properties of Fuel Oxygenates Relative to Benzene

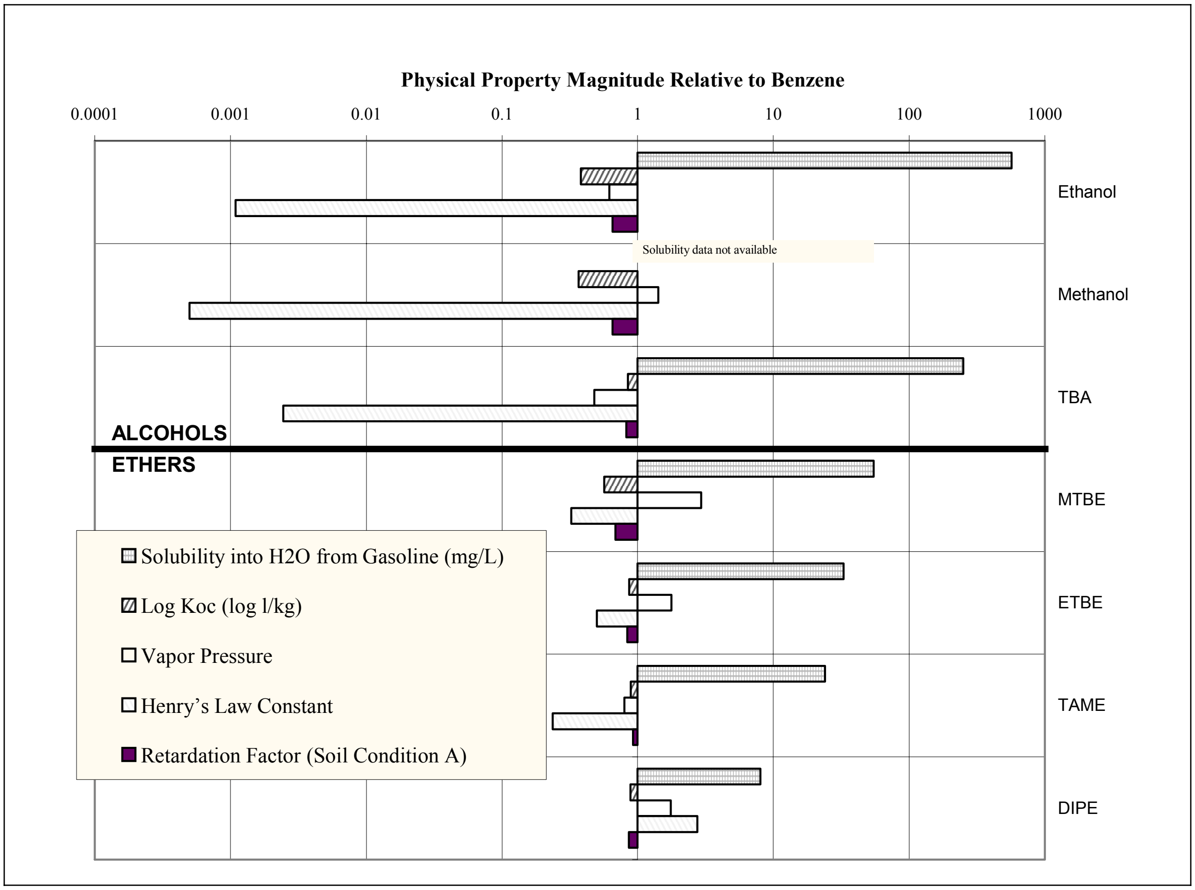
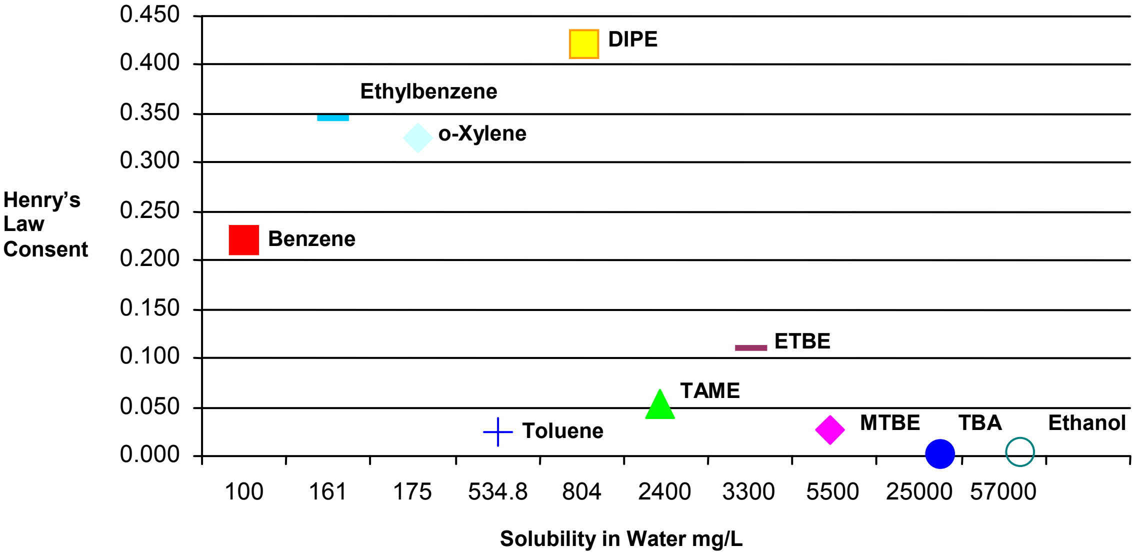


Figure 2-3. Relative Solubility and Henry's Law Constants for Selected Fuel Oxygenates (Henry's Law data for MtBE, TBA, and Benzene based on Zogorski et. al., 1997)



2.8 What Types of Technologies are Used in the Treatment of Soil, Groundwater, and Drinking Water Contaminated with Oxygenates?

Technologies that have been used to treat groundwater and soil contaminated with oxygenates include air sparging, SVE, MPE, *in situ* bioremediation, *in situ* chemical oxidation (ISCO), groundwater extraction and above-ground treatment (i.e., pump-and-treat or drinking water treatment), and phytoremediation. Above-ground treatment for extracted groundwater includes technologies such as air stripping, activated carbon, chemical oxidation, and bioremediation. Air sparging, SVE, and MPE rely generally on the use of air flow to remove contaminants, and are discussed before the other technologies. Bioremediation and ISCO rely on biological and chemical reactions to destroy MtBE and other oxygenates, while pump-and-treat and drinking water treatment rely primarily on physical and chemical parameters to separate MtBE and oxygenates from water. Other technologies discussed in this report, such as phytoremediation, *in situ* thermal treatment, and permeable reactive barriers, have also been used at sites contaminated with oxygenates, although less often at the sites in EPA's MtBE database. Non-treatment remedies that have been used include excavation, free product recovery, monitored natural attenuation (MNA) and institutional controls (IC). These technologies are discussed in more detail in Sections 4 and 5 of this report.

Additional sources of information that discuss treatment of MtBE using multiple technologies include the following:

- Moyer, E.E. and Kostecki, P.T., Eds. 2003. *MtBE Remediation Handbook.* AEHS. Amherst Scientific Publishers.
- Evaluation of MTBE Remediation Options. 2004. The National Water Research Institute. April. www.nwri-usa.org/.

2.9 How Are Technologies Used to Treat Soil and Water Contaminated with Oxygenates?

Remediation of a site contaminated with MtBE and other fuel oxygenates is often conducted using a phased approach. Often, the first phase of remedial action at a site focuses on protecting receptors at the site, such as nearby buildings or drinking water supplies. The second phase generally involves controlling the source of the contamination, for example excavation of leaking underground storage tanks (USTs) or contaminated soil, or free product removal. The next phase typically involves the active cleanup of residual and dissolved contamination using one or more treatment technologies. Active cleanup of residual and dissolved contamination often is followed by MNA (Jansen et. al., 2002).

Technologies might be applied sequentially or simultaneously in different parts of a contaminated site, depending on the concentration of oxygenates and potential risks to receptors. For example, at a gasoline service station site with a leaking UST, excavation, free product removal, or SVE might be performed at the source area; air sparging, *in situ* chemical oxidation, or *in situ* bioremediation in the plume area (these technologies could also be used for source area treatment at some sites); or pump-and-treat as the plume gets closer to a receptor. If concentrations are sufficiently low, MNA might be used instead of an active bioremediation technology or pump-and-treat for the residual plume. When considering MNA as a potential remedy, remediation timeframe is an important factor to consider. Treatability studies (bench- or pilot-scale) often are performed to evaluate how a technology would perform on the actual soil or groundwater at a site. The results of these studies are used in preparing a design for full-scale remediation (EPA, 1999b).

2.10 What Additional Technical Considerations are Associated with Remediating Sites Contaminated with Oxygenates?

Other technical considerations related to remediation of sites contaminated with MtBE and oxygenates include contaminant concentration, cleanup goals, presence of other contaminants at the site, and site-specific considerations that may affect the selection and design of treatment technologies. There tends to be wide variability in the range of concentrations of MtBE or other oxygenates in soil and groundwater at sites. The concentration of MtBE in contaminated groundwater and soil for the projects reviewed for this report ranged from 5 to 1,000,000 µg/L. In addition, soil and groundwater treatment goals for MtBE-contaminated sites are currently based on state-specific standards and risk-based levels that range from 5 to 280,000 µg/L in soil and from 5 to 200,000 µg/L in groundwater. State-established primary drinking water limits for MtBE range from 5 to 240 µg/L (Delta Environmental Consultants, Inc., 2004). High contaminant concentrations at sites with low cleanup goals can result in the need for treatment technologies and system designs able to achieve higher removal efficiencies and more aggressive remediation.

Many other factors can affect the performance and cost for implementing a technology at a given site, including the nature and extent of contamination, depth of contamination, physical and chemical characteristics of a site (such as dimensions and hydrogeology), design and operation of a treatment system, regulatory requirements, and logistical issues. Typically, these factors are quantified before an engineering level design is made for use of a technology at a given site.

In addition, it is important to recognize that sites with spilled or leaked gasoline contain 200-300 distinct chemicals which can contaminate soil and groundwater; approximately 6-10% of the spilled/leaked gasoline typically consist of fuel oxygenates such as MtBE (McGarry, 2002).

3.0 COMPARISON OF TREATMENT TECHNOLOGIES

This section contains a comparison of the following nine technologies that have been used to treat sites contaminated with MtBE and other fuel oxygenates:

- Air Sparging
- Soil Vapor Extraction (SVE)
- Multi-Phase Extraction (MPE)
- *In Situ* Bioremediation
- *In Situ* Chemical Oxidation (ISCO)
- Pump-and-Treat
- Other Treatment Technologies
    - Phytoremediation
    - Permeable Reactive Barriers
    - *In Situ* Thermal Treatment

The information used for this comparison is based primarily upon information reported for 323 MtBE remediation technology projects at EPA's MtBE Treatment Profile Website, available at www.cluin.org/products/mtbe, as well as information available from published literature sources. This section provides a summary overview of these technologies and Section 4 includes more detailed information related to each individual technology, including a technology description, a discussion of how the properties of fuel oxygenates affect treatment, and more detailed information summaries related to the 323 projects in the dataset.

3.1 What Types of Remediation Technology Projects were Considered in this Comparison?

Information about 323 MtBE remediation technology projects was reviewed during the preparation of this report. These projects employed primarily air sparging, SVE, MPE, bioremediation, ISCO, and pump-and-treat to remediate MtBE and other oxygenates in groundwater and soil. Some sites also used phytoremediation, PRBs, or *in situ* thermal treatment. Table 3-1 summarizes the number of projects that used each of these technologies, as well as the scale (full-scale, pilot-scale, or bench-scale) and status (completed or ongoing) of the projects reviewed, and the number of projects for which performance and cost data were available. Among the six technologies, air sparging, SVE, bioremediation, and pump-and-treat were used more frequently to remediate groundwater and soil contaminated with MtBE and other oxygenates, and MPE, ISCO, phytoremediation, PRBs, and thermal treatment were used less frequently. Nearly 25 percent of the projects have been completed, with the remaining 75 percent ongoing. Eighty percent of the projects provided some type of performance data, and more than 30 percent provided cost data. Performance and cost data were provided most often for projects using air sparging, bioremediation, and pump-and-treat.

Table 3-1. Description of MtBE Remediation Technology Projects (323 Projects)

Technology	Number of Projects	Project Scale			Project Status		# of Projects with Performance Data	# of Projects with Cost Data
		Bench	Pilot	Full	Com-pleted	On-going		
Air Sparging	123	1	2	120	19	104	113	39
Soil Vapor Extraction	138	0	1	137	19	119	129	24
Multi-Phase Extraction	13	0	4	9	4	9	10	2
Bioremediation	73	7	13	53	35	38	68	28
In situ Chemical Oxidation	21	0	4	17	8	13	20	2
Pump-and-treat	100	0	16	84	22	78	76	43
Phytoremediation	8	3	4	1	5	3	1	0
Permeable Reactive Barriers	6	0	2	4	4	2	4	0
Thermal Treatment	1	0	0	1	1	0	1	0

Note: Each project may involve use of one or more than one specific technology.

Source: EPA, 2002a

3.2 How Did These Remediation Technologies Perform?

As shown on Table 3-1, performance data were available for all 323 of the MtBE remediation projects in the dataset. However, most of these projects with performance data are ongoing. To evaluate performance of specific technologies and projects, 105 completed projects with performance data were identified, along with the minimum, median, and maximum of the highest concentration of MtBE measured in the groundwater before treatment (initial) and after treatment (final), as shown in Table 3-2. Limited performance data were available about the projects that employed phytoremediation, PRBs, and thermal treatment, and are not presented in this table. A summary of the technology-specific data for these technologies is included in Section 4, with project-specific data provided in Appendix A.

Table 3-2. Performance Data for Completed MtBE Remediation Technology Applications (105 Applications[1] Providing Data)

Technology	# of Completed Projects with Performance Data	Initial MtBE Concentration [2] (µg/L) in Groundwater			Final MtBE Concentration [2] (µg/L) in Groundwater		
		Minimum	Median	Maximum	Minimum	Median	Maximum
Air Sparging	19	5	2,100	62,000	2	16	2,070
Soil Vapor Extraction	23	5	2,600	44,400	2	21	3,200
Multi-Phase Extraction	3	11	55	6,140	79	435	791
Bioremediation	35	5	3,880	100,000	<1	30	33,000
In situ Chemical Oxidation	8	55	11,700	475,000	5	75	68,400
Pump-and-Treat	21	3	1,610	475,000	<1	11	68,400

Notes:

1 For projects where more than one technology was used, performance information is presented under each of the technologies used for the project.

2 MtBE concentrations for all technologies are reported for groundwater. For technologies that affect soil (such as MPE and SVE), source materials provided information on MtBE concentrations in groundwater. For all projects, the highest concentration reported prior to beginning treatment (shown as “initial”) and the highest concentration after treatment was completed (shown as “final”) is provided.

Source: EPA, 2002a

As discussed in Section 1, these performance data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website. There was variation among the profiles in the level of detail for performance data. Many of the treatment profiles contained only limited information about treatment performance, generally including a maximum concentration of MtBE before-treatment and a maximum concentration of MtBE after-treatment. Most treatment profiles did not provide detailed performance data, such as MtBE concentration over the duration of the project, or statistical evaluations of performance data with confidence limits.

As mentioned before, treatment performance is site-specific and dependent on many factors; thus it is difficult to extrapolate from one site to another. The data are provided to give a general indication of technology performance. These factors include site conditions (such as soil types, permeability, conductivity, redox conditions, and degree of heterogeneity), technology design and operation, and regulatory considerations, such as cleanup levels. Additional factors include duration of the release (such as a gasoline leak), presence of down-gradient water supply wells, and distribution of contaminants in soil and groundwater.

Table 3-3 summarizes the duration of 89 completed remediation projects. Although project duration is dependent on a number of factors, such as extent of contamination and cleanup levels, the data from these 89 projects show a relatively shorter median duration for projects using bioremediation or ISCO, compared with those using air sparging, SVE, pump-and-treat, or MPE.

Table 3-3. Duration of Completed MtBE Remediation Technology Applications (89 Applications Providing Data)

Technology	# of Projects	Project Duration (months)		
		Minimum	Median	Maximum
Air Sparging	18	3	22	75
Soil Vapor Extraction	22	3	21	66
Multi-Phase Extraction	1	45		
Bioremediation	24	<1	6	60
In situ Chemical Oxidation	7	2	12	18
Pump-and-Treat	17	<1	31	75

Notes:

1 For projects where more than one technology was used, information is presented under each of the technologies used for the project.

Source: EPA, 2002a

3.3 What Did These Remediation Technologies Cost?

Table 3-4 summarizes the cost information reported for 127 MtBE remediation technology applications. Only costs reported as total project costs are summarized in this table. Note that these include both completed and ongoing projects. Because of the wide variation in the components that were included in the reported total project costs, these data should only be used as a general reference about costs and should not be used as a sole basis to estimate costs for future MtBE remediation projects or to compare the cost of technologies. Additional information about the costs reported for the remediation technologies are provided in Section 4.

Table 3-4. Total Project Cost[1] Data for MtBE Remediation Technology Applications (127 Applications Providing Data)

Technology	# of Projects with Cost Data	Total Project Costs Reported ($)		
		Minimum	Median	Maximum
In situ Chemical Oxidation	2	$60,000	$103,000	$146,000
Bioremediation	30	$4,000	$137,000	$5,200,000
Soil Vapor Extraction	24	$14,700	$206,000	$4,600,000
Air Sparging	39	$13,700	$247,000	$1,050,000
Multi-Phase Extraction	2	$130,000	$257,000	$383,000
Pump-and-Treat	43	$65,000	$327,000	$4,000,000

Note:

1 For projects where more than one technology was used, cost information is presented under each of the technologies used for the project. Table includes total costs for completed projects, and costs to date for ongoing projects. Projects were of varying sizes, concentrations, and other site conditions. A summary of project-specific data for these technologies is provided in Appendix A.

2 Total project cost included more than just the treatment cost, such as cost for ancillary treatment processes, monitoring costs, or source removal costs. The costs summarized in this table have not been normalized to account for the types of cost components included, locations of the projects, or the time when the costs were incurred (inflation factors, see EPA 2001c). For a majority of the applications, reported costs were based on actual incurred costs. However, for some applications, costs were estimated as projected full-scale costs based on a scale up of pilot- or bench-scale projects.

Source: EPA, 2002a

In addition, EPA recently prepared a more detailed analysis of treatment cost for *in situ* treatment of fuel oxygenates. The paper, “Cost of *In Situ* Treatment of Fuel Oxygenates”, was presented at the National Ground Water Association conference on Remediation: Site Closure and the Total Cost of Cleanup, New Orleans, held November 13-14, 2003, and is available at www.cluin.org/mtbe.

As discussed earlier for performance data, the cost data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website. There was variation among the profiles in the level of detail for cost data by project, with many of the treatment profiles containing only limited information about treatment cost. Treatment cost is site specific and depends on many of the same factors that also affect performance, such as site conditions, project scale, technology design and operation, and regulatory considerations. Therefore, these cost data are intended to give a broad indication of the types of costs associated with cleanup projects, and users should be cautious about drawing conclusions about the cost of cleanup projects at specific sites based on these data. As discussed later in the report, very few projects provided sufficient information to calculate a unit cost for treatment.

For some of the treatment profiles, the specific components that make up the total cost were not provided in the source materials, such as for capital or operation and maintenance [O&M] activities. In other cases, the types of contaminants present at the sites, other than MtBE, were not identified in the source materials. Sites may have been contaminated with gasoline components such as petroleum hydrocarbons, as well as oxygenates, and the treatment costs reported are for cleanup of both the gasoline components as well as the oxygenates. For example, for a specific project, most of the cost for cleanup may be due to gasoline components other than oxygenates.

Costs for most of these projects were provided as a total remedial cost. Some projects also included the cost for ancillary treatment processes, monitoring costs, or source removal costs in the total cost. For most of the projects, reported costs were based on actual incurred costs. For other projects, costs were estimated as projected full-scale costs based on a scale up of pilot-scale projects or on engineering estimates. Because most of the costs for use of the treatment technologies are related to system design, installation, and startup, these partial or estimated costs may be relatively close to the eventual total project cost. However, the reported project costs should still be considered estimates because the cost components for each project are not consistent and it is possible that significant costs could be associated with system operation, maintenance, monitoring, and decommissioning. In addition, these cost data were not normalized to account for the project year or location. (Further information about normalizing cost data is provided in EPA 2001c).

3.4 What Factors Should Be Considered When Identifying Technologies to Treat Fuel Oxygenates?

Table 3-5 summarizes the general factors to be considered when identifying technologies to treat sites contaminated with fuel oxygenates. These general factors were developed based on data from the 323 technology applications, as well as from the *Remediation Technology Screening Matrix and Reference Guide* published by the Federal Remediation Technologies Roundtable (FRTR), and other industry references. As shown in Table 3-5, these general factors include type of treatment, relative time to complete, and relative cost.

Table 3-5. General Factors to Consider When Identifying a Remediation Technology for Sites Contaminated with Fuel Oxygenates

Technology	Type of Treatment			Relative Time to Complete	Relative Cost
	In situ*/ *Ex situ	**Media**	**Source/ Plume**		
Air Sparging	In situ	GW	Plume	Average	Average to Lower
Soil Vapor Extraction	In situ	Soil	Source	Average to Longer	Lower
Multi-Phase Extraction	In situ	Both	Source	Average	Average to Higher
In situ Bioremediation	In situ	Both	Plume	Average to Shorter	Lower
In situ Chemical Oxidation	In situ	Both	Source	Shorter	Average to Lower
Pump-and-Treat	Ex situ	GW	Plume	Longer	Higher
Phytoremediation	In situ	Both	Plume	Longer	Lower
Permeable Reactive Barriers	In situ	GW	Plume	Longer	Lower
In situ Thermal Treatment	In situ	Both	Source	Shorter	Average

Source: EPA 2002a and FRTR 2002

Table 3-6 summarizes some of the general factors that are often considered when selecting a remediation technology for sites contaminated with fuel oxygenates. These include potential benefits (such as minimal site disturbance, integration with other treatment technologies, or applicability to challenging site conditions) and limitations (such as types of contamination not suited to treatment, undesired migration or transformation of contamination, or health and safety considerations). A more detailed discussion of specific factors for each technology is provided in Section 4.

Table 3-6. General Factors to Consider When Selecting a Remediation Technology for Sites Contaminated with Fuel Oxygenates

Technology	Potential Benefits	Potential Limitations
Air Sparging	• Causes minimal disturbance to site operations • Addition of oxygen to the subsurface may enhance aerobic biodegradation • Can be a cost-effective alternative for sites with groundwater contamination	• May cause a lateral spread of dissolved or separate phase contaminant plume • Contamination may be transferred from groundwater to the vadose zone • Has limited applicability at sites with confined aquifers
SVE	• Reduces the potential for migration of vapors into buildings or leaching into groundwater • Causes minimal disturbance to site operations • Can be a cost-effective alternative for sites with soil contamination and, in some cases, free product	• Low soil permeability or other heterogeneous conditions may reduce effectiveness • Shallow depths to groundwater or fluctuations in groundwater table can cause upwelling and interference with airflow • Off-gas typically requires treatment
MPE	• May increase groundwater recovery rates, compared to conventional pumping practices in equivalent settings • Can be used to recover free product • May be used to remediate the capillary fringe and smear zone • Can be a cost-effective alternative for sites with contamination in both soil and shallow groundwater	• NAPL emulsions and VOC-laden vapors may increase treatment requirements • Initial start-up and adjustment periods may be relatively long • Some MPE configurations have depth limitations • Off-gas typically requires treatment
In situ Bioremediation	• Causes minimal disturbance to site operations • Often biodegradation can be enhanced by use of other technologies, such as air sparging, SVE, MPE, thermal, or ISCO • Can be a cost-effective alternative for sites with contamination in both soil and groundwater	• Presence of other organic contaminants may inhibit biodegradation • Degradation pathways for anaerobic processes not as well understood as aerobic pathways; anaerobic processes typically slower • High concentrations of contaminants may be toxic and/or not bio-available • May be difficult to implement in low-permeability aquifers • Re-injection wells or infiltration galleries may require permits or may be prohibited • Biodegradation pathways may be site-specific, potentially requiring pilot testing or treatability studies
In situ Chemical Oxidation	• Can be a cost-effective alternative for hot spots that may not be amenable to bioremediation • Contaminants are treated rather than transferred to a vapor phase • Causes minimal disturbance to site operations	• Relatively large amount of oxidant may be needed for treatment of large contaminant mass • May be low contact between oxidant and contaminant in heterogeneous conditions or in areas with low permeability • Special precautions may be needed to protect worker health and safety during operation • Oxidation reactions may form toxic by-products in the groundwater or in off-gases and off-gas may require capture and treatment

Technology	Potential Benefits	Potential Limitations
Pump-and-Treat	- Can be a cost-effective alternative to treat an aquifer or to provide hydraulic containment for sites contaminated with fuel oxygenates	- May require an extended operation and maintenance period - Cost of constructing, operating, and maintaining treatment system can be relatively high - Biofouling of extraction wells can reduce system performance - The typical design of common above-ground treatment systems may not be effective for oxygenates
Phytoremediation	- Can be a cost-effective alternative for remediating or containing relatively low concentration, shallow, and widespread soil or groundwater plumes	- Limited information available about the specific processes used in phytoremediation that reduce concentration of fuel oxygenates - Typically lengthy startup period - Phytoremediation generally less applicable to higher concentrations or deeper groundwater plumes
Permeable Reactive Barriers	- Can be a cost-effective alternative for preventing the migration of contaminated groundwater plumes	- May affect natural groundwater flow gradients at a site, potentially resulting in lateral or vertical migration of the contaminant plume - Requires a high degree of engineering for design and installation
In situ Thermal Treatment	- Can be a cost-effective alternative for remediating source areas in soil or groundwater - Tends to remove oxygenates when used to treat other petroleum contaminants (such as petroleum hydrocarbons)	- May not be cost-effective for use at small sites such as service stations - Requires a high degree of engineering for design, installation, and operation

Sources: EPA 2002a and FRTR 2002

For practitioners of *in situ* technologies, note that EPA has issued a policy statement that reinjection of contaminated groundwater is allowed under RCRA section 3020(b) as long as certain conditions are met. This policy is intended to apply to remedies involving *in situ* bioremediation and other forms of *in situ* treatment. Under this policy, groundwater may be reinjected if it is treated aboveground prior to reinjection. Treatment may be by a "pump-and-treat" system or by the addition of amendments meant to facilitate subsurface treatment. Also the treatment must be intended to substantially reduce hazardous constituents in the groundwater (either before or after reinjection); the cleanup must be protective of human health and the environment; and the injection must be part of a response action intended to clean up the environment (EPA, 2000f).

4.0 TREATMENT TECHNOLOGIES

This section summarizes available information on nine treatment technologies that have been applied to treat MtBE and other oxygenates in groundwater, soil, and drinking water. Table 4-1 provides a brief description of these technologies, along with each technology's applicability to treat groundwater, soil, or both to treat oxygenates either *in situ* or *ex situ.* Groundwater contaminated with MtBE has most often been treated using air sparging, bioremediation, ISCO, pump-and-treat, and MPE. To date, soil contaminated with MtBE has been treated primarily with SVE. Drinking water contaminated with MtBE and other fuel oxygenates is typically treated using the same aboveground treatment technologies associated with pump-and-treat, such as air stripping, adsorption, chemical oxidation, or bioremediation. In addition to these treatment technologies, several non-treatment remedies (excavation, product recovery, and monitored natural attenuation) have been used to enhance MtBE source removal or plume management remedies and are discussed in Section 5. The remainder of this section provides information summarized from 323 MtBE-remediation technology applications (based primarily on EPA MtBE Treatment Profiles – see Section 1) that can assist in remedy selection at sites contaminated with MtBE and other fuel oxygenates.

Table 4-1. Types of Technologies Used to Treat MtBE and Other Fuel Oxygenates

Section	Treatment Technology	Ground water	Soil	*In Situ* or *Ex situ*	Description
4.1	Air Sparging	●		*In situ*	Injection of air into the groundwater to strip out VOCs
4.2	SVE		●	*In situ*	Application of a vacuum to the soil to extract VOCs and treatment using aboveground processes
4.3	MPE	●	●	*In situ*	Simultaneous extraction of VOCs from soil and free product/groundwater and treatment using aboveground processes
4.4	*In situ* Bioremediation	●	●	*In situ*	Addition of oxygen or other amendments to stimulate and enhance biodegradation
4.5	*In situ* Chemical Oxidation	●	●	*In situ*	Injection of chemicals such as ozone, hydrogen peroxide, or permanganate into the subsurface to oxidize contaminants
4.6	Groundwater Extraction for Pump-and-Treat and Drinking Water Treatment	●		*Ex situ*	Extraction of contaminated groundwater for treatment prior to use or disposal
4.7	Above-Ground Treatment Technologies for Extracted Groundwater	●		*Ex situ*	Treatment of extracted groundwater using *ex situ* processes such as air stripping, adsorption, biological reactors, or oxidation
4.8	PRBs	●		*In situ*	Placement of a reactive zone that treats contaminants as groundwater flows through the zone
	Phytoremediation	●	●	*In situ*	Use of trees and other higher plants to remove or destroy contaminants
	In situ Thermal Treatment	●	●	*In situ*	Use of heat to mobilize or destroy contaminants

4.1 Air Sparging

Overview

- Injection of air into the groundwater to strip out volatile contaminants
- EPA's MtBE Treatment Profiles dataset includes use at 123 sites to treat MtBE, often in conjunction with SVE
- Some oxygenates may be less amenable to air sparging than other volatile contaminants

4.1.1 What is Air Sparging?

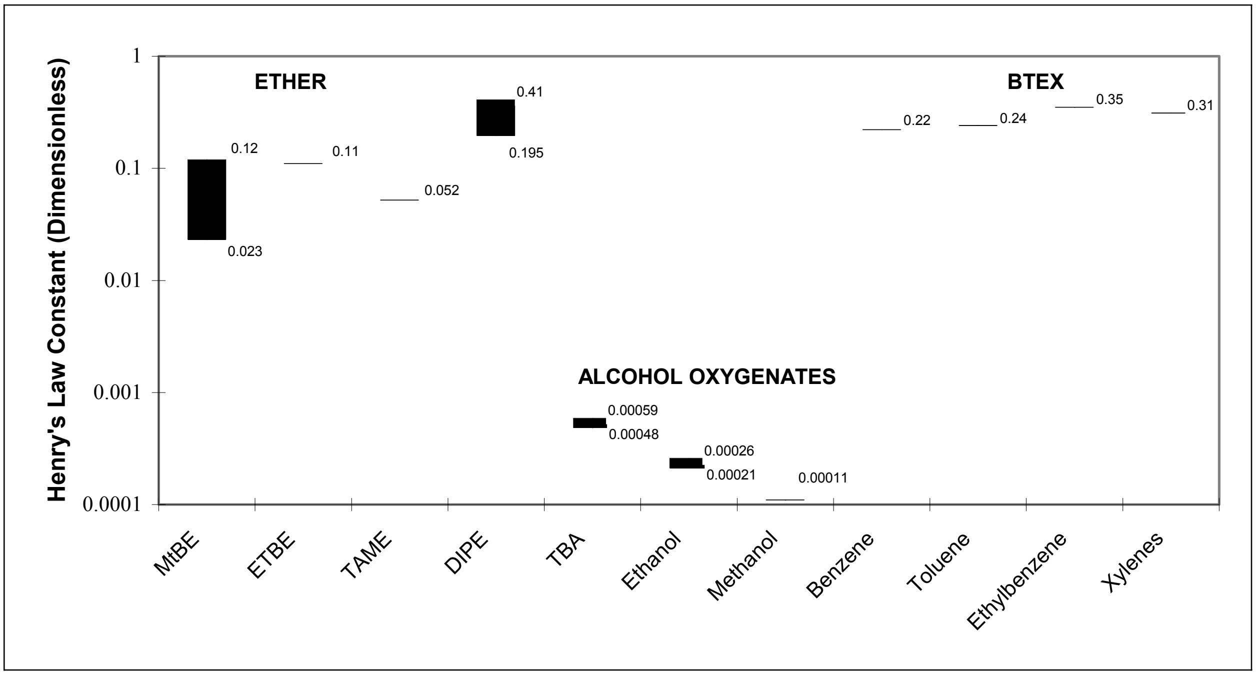
Air sparging is an *in situ* technology that removes VOCs such as MtBE and other oxygenates from the groundwater through the injection of air, which induces a phase transfer of VOCs from a dissolved state to a vapor state that can be extracted from the subsurface or allowed to attenuate in the vadose zone. During air sparging, biodegradation of contaminants (including MtBE and other oxygenates) can also be promoted by the oxygen in the injected air. In some cases, pure oxygen or air amended with other gases, such as triethylphosphate (a nutrient), or butane or propane (cometabolic substrates), are injected to further promote biodegradation of contaminants. For the purpose of this report, technology applications that rely on biodegradation as a primary pathway for contaminant remediation are considered to be bioremediation projects, and are discussed in more detail in Section 4.4.

4.1.2 How Do the Properties of MtBE and Other Oxygenates Affect Treatment?

In an air sparging system, the primary mechanism for contaminant removal is the transfer of contaminants from the dissolved to the vapor phase. The extent to which this transfer can take place during air sparging depends on the Henry's Law Constant, which is an indication of the extent to which each will partition between the dissolved state and the vapor state under equilibrium conditions. A contaminant with a greater Henry's Law Constant is more readily stripped from groundwater by air sparging than one with a lower Henry's Law Constant.

Figure 4.1-1 shows the Henry's Law Constants for the common fuel oxygenates. The Henry's Law Constants in this table are shown as dimensionless values representing the ratio of the concentration in the vapor state compared to its concentration in the aqueous state at 25˚C. As shown on the table, all of the common oxygenates (with the possible exception of DIPE) have Henry's Law Constants that are lower than those for benzene, toluene, ethylbenzene, and xylene (BTEX), which range from 0.22 for benzene to more than 0.3 for xylene. Because of this, an air sparging system designed to remediate BTEX may not adequately address oxygenates. Research has shown that the removal of MtBE requires 5 to 10 times more airflow than would have been used for BTEX alone (Fields et al., 2001). In addition, the ether-based oxygenates have Henry's Law Constants that are about two to three orders of magnitude greater than those for alcohol-based oxygenates, suggesting that ether-based oxygenates, such as MtBE, can be removed more readily using air sparging than alcohol-based oxygenates, such as TBA. However, alcohol-based oxygenates may be more readily biodegraded (see Section 4.4) or may have less stringent (higher concentration) cleanup goals at some sites than ether-based oxygenates. Thus, it is possible that air sparging could be used to remediate sites contaminated with both alcohol-based and ether-based oxygenates.

Figure 4.1-1. Ranges of Henry's Law Constants (Dimensionless) for Common Fuel Oxygenates



Notes:

1. Henry's Law Constants shown as dimensionless values representing the ratio of the concentration in the vapor state compared to its concentration in the aqueous state at 25˚C.
2. Data from "Guidelines for Investigating and Cleanup of MtBE and Other Ether-Based Oxygenates", CalEPA, State Water Resources Control Board, March 2000.

4.1.3 How is Air Sparging Applied to Treat Oxygenates?

During air sparging, compressed air is forced into the saturated zone through one or more injection points, such as vertical or horizontal wells or engineered trenches, screened beneath the water table. The injected air flows and rises through the saturated zone. As the injected air passes through groundwater containing dissolved volatile contaminants, these contaminants partition to the injected air based on their individual physical properties. In addition, oxygen present in the injected air will dissolve into the groundwater at the gas-water interface and diffuse into the surrounding groundwater, potentially stimulating biodegradation of contaminants. When the injected air reaches the vadose zone, it can be extracted using SVE. Extracted vapors may be treated using aboveground technologies (Section 4.2 discusses SVE and aboveground vapor treatment technologies) or is allowed to attenuate naturally in the vadose zone through dispersion and biodegradation. Air sparging has been used without SVE when contaminant concentrations are relatively low or potentially affected receptors are far from the area being treated (Symons and Greene, 2003).

The design and configuration of air sparging systems to treat oxygenates varies widely based on site-specific conditions and is typically established through pilot-scale testing to determine the radius of influence (ROI) or zone of influence (ZOI) of an air sparging well under site conditions. The ROI or ZOI is the area around an injection well where there is adequate sparge pressure and airflow to enhance the transfer of contaminants from the dissolved phase to the vapor phase. Spacing between air sparging wells typically ranges from 5 to 40 feet (ft), depending on the surrounding soil characteristics, and airflow rates commonly range from 1 to more than 40 standard cubic ft per minute (scfm). Pilot testing is typically employed to determine an appropriate airflow rate (maximizing the ROI/ZOI while limiting the potential for unintended subsurface fracturing and over-mobilization of the contamination) for a given site. The flow of air through the sparging wells can be continuous or pulsed. Pulsed systems have been shown to increase mass transfer removal in some instances (EPA, 1995; FRTR, 2002; USACE, 1997).

More detailed information relevant to the application of air sparging at sites in general or those contaminated with MtBE and other fuel oxygenates is available in the following documents:

- Symons, Brian D., and J. Greene. 2003. “Soil Vapor Extraction, Bioventing, and Air Sparging”. In Moyer and Kostecki, Eds. 2003. *MtBE Remediation Handbook.* Amherst Scientific Publishers.
- Naval Facilities Engineering Service Center. 2001. *Final Air Sparging Guidance Document*. NFESC Technical Report TR-2193-ENV. August 31.
- U. S. Environmental Protection Agency. 2001. *Development of Recommendations and Methods to Support Assessment of Soil Venting Performance and Closure.* EPA 600-R-01-070.
- U.S Army Corps of Engineers. 1997. *USACE Engineering Manual: In Situ Air Sparging.* EM 1110-1-4005. September 15.
- American Petroleum Institute. 1995. *In Situ Air Sparging: Evaluation of Petroleum Industry Sites and Considerations for Applicability, Design and Operation*. Product Number I46090. May.

4.1.4 What Types of Projects Involve Air Sparging for Oxygenates?

From the 323 projects in EPA’s MtBE Treatment Profiles dataset, 123 projects were identified where MtBE was treated using air sparging alone or in conjunction with another technology. Information on the treatment of other fuel oxygenates during these 123 projects is limited; one project also reported TBA as a co-contaminant and another project reported TBA and ethanol as co-contaminants.

Table 4.1-1 summarizes the scale and operational status for the 123 air sparging projects. The data used to compile this information was current at the time the profile for each project was compiled. It is possible that some projects shown as ongoing may now be completed. Short summaries for two projects, *Air Sparging at Exxon and Mobil Service Stations in Smithtown, NY* and *Air Sparging at Eaddy Brothers Service Station in Hemingway, SC*, are included at the end of this section, with additional information about all 123 projects provided in Appendix A.

Table 4.1-1. General Information on 123 Air Sparging Projects

Technology(ies)	# of Projects	Operational Status		Scale		
		Completed	Ongoing	Bench	Pilot	Full
Air Sparging Only	13	3	10	0	1	12
Air Sparging with SVE	74	2	72	0	0	74
Air Sparging with Pump-and-Treat	4	2	2	0	0	4
Air Sparging with SVE and Pump-and-treat	19	5	14	0	0	19
Air Sparging with Multiple Technologies	13	7	6	1	1	11
TOTAL	**123**	**19**	**104**	**1**	**2**	**120**

As shown in Table 4.1-1, most of the 123 air sparging projects were conducted at full scale (120 projects) and were ongoing (104 projects) at the time the profile was prepared. In addition, while most (87) of the projects used air sparging alone or in conjunction with SVE, 36 projects supplemented air sparging treatment with pump-and-treat or other technologies, such as MPE, bioremediation, free product recovery, and ISCO.

The 123 air sparging projects primarily used vertical wells; three projects reported use of horizontal wells. For 69 projects for which information about the number of air sparging wells was available, 48 used 2 to 8 wells per project, with a range of 1 to 30 wells. One project identified an ROI (27 ft). Three projects reported continuous airflow, two reported pulsed flow, and the remainder provided no information on the type of airflow. For the 74 projects that used air sparging with SVE, the number of SVE wells used ranged from 1 to 23 wells per project, with 30 projects in the range of 2 to 5 wells per project. Four of these 74 projects reported the type of air emission treatment used, with two reporting use of GAC, one of catalytic oxidation, and one of thermal oxidation.

4.1.5 How Has Air Sparging Performed in Treating Oxygenates?

The treatment performance data for 123 projects presented in Tables 4.1-2 and 4.1-3 show that air sparging (either alone or in combination with other technologies) has been used to reduce MtBE in groundwater from concentrations greater than 1,000,000 µg/L to less than 50 µg/L. The median project duration for the 19 completed sites ranged from 1 to 5 years. Although 2 of the 123 projects listed TBA as a co-contaminant, neither of these projects reported TBA concentrations before or after treatment; no data for other fuel oxygenates was reported.

Table 4.1-2. Completed Air Sparging Projects - Performance Summary for 19 Projects

Technology(ies)	# of Projects	Initial MtBE Concentration [1] (µg/L)			Final MtBE Concentration [1] (µg/L)			Median Project Duration (months)
		Minimum	Median	Maximum	Minimum	Median	Maximum	
Air Sparging Only	3	230	1,600	62,000	5	27	980	18
Air Sparging with SVE	2	99	218	337	NR			57
Air Sparging with Pump-and-Treat	2	1,200	6,100	11,000	16	1,040	2,070	43
Air Sparging with SVE and Pump-and-Treat	5	5	203	2,600	2	3	5	50
Air Sparging with Multiple Technologies	7	55	7,940	44,400	79	79	79	18

Notes:

NR Information not provided

[1] Treatment performance data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website, as shown in cluin.org/products/mtbe, and summarized in Appendix A. Appendix A shows the specific sites that are summarized here, along with technology design, operation, and performance data for each of the projects.

[2] Performance data are shown in terms of changes in concentration of MtBE in the groundwater, as provided in the reference materials and from the project contacts, except as noted. MtBE concentrations prior to beginning treatment (shown as "initial concentration") and after treatment was completed (shown as "final concentration") are provided. For projects where more than one technology was used, performance data are presented under each of the technologies used for the project.

Table 4.1-3. Ongoing Air Sparging Projects – Performance Summary for 104 Sites

MtBE Concentration Range	# of Projects Reporting Initial MtBE Concentrations	# of Projects with Last Reported MtBE Concentrations
Greater than 100,000 µg/L	4	1
Greater than or equal to 10,000 µg/L but less than 100,000 µg/L	16	3
Greater than or equal to 1,000 µg/L but less than 10,000 µg/L	24	10
Greater than or equal to 100 µg/L but less than 1,000 µg/L	25	20
Greater than or equal to 50 µg/L but less than 100 µg/L	4	5
Less than 50 µg/L	18	15

4.1.6 What Costs Have Been Associated with Using Air Sparging in Treating MtBE?

Project cost data were reported for 39 of the 123 air sparging projects in the dataset; these include data for both ongoing and completed projects. In most cases, the components that make up the project costs were not reported. However, other components, such as treatment, monitoring, design, oversight, and health & safety, may be included in the cost. Most (38 projects) of the reported costs were for ongoing projects and represent either a partial actual cost as of the time that the report was made or an estimated total project cost.

The median reported total cost for all air sparging projects was approximately $250,000, with most projects having a total cost between $100,000 and $350,000. For 7 of these projects that used air sparging alone, the total cost ranged from $20,000 to $345,000 per project. For the 17 projects that used air sparging with SVE, the total cost ranged from $27,000 to $1,051,000 per project. The total cost for 15 of the projects ranged from $96,000 to $672,000 per project.

Because the area, volume, or mass treated was not consistently available for the 39 air sparging projects, no unit costs were calculated. The cost per volume of groundwater treated (identified as tons of saturated soil) was reported in one literature source as ranging from $20 to $50 per ton of saturated soil for air sparging in general (EPA, 1995). Another source identified the unit cost as $371,000 to $865,000 per hectare ($150,000 to $350,000 per acre) of groundwater plume treated for air sparging in general (FRTR, 2002). The cost of air sparging generally is considered to be better than average, among the costs for remediation technologies, for treatment of contaminated groundwater (FRTR, 2002). Because of the relative airflow requirements necessitated by the lower Henry's Law Constants of MtBE and other oxygenates, the unit costs for the remediation of sites contaminated with MtBE and other oxygenates could be at the upper end of these ranges.

4.1.7 What Factors May Affect the Performance and Cost of Oxygenate Treatment Using Air Sparging?

Because ether- and alcohol-based oxygenates exhibit different properties (specifically, Henry's Law Constant) than other common fuel contaminants such as BTEX, their presence may affect the size and design of the air sparging system required to remediate the site and, as a result, the cost of remediation. Research has shown that the removal of MtBE (ether-based) requires 5 to 10 times more airflow than used for BTEX alone (Fields, et al., 2001). The other common ether-based oxygenates have higher Henry's Law Constants than MtBE and are theoretically more amenable to treatment via air sparging (although still less amenable than BTEX components). The common alcohol-based oxygenates have Henry's Law Constants two to three orders of magnitude lower than those of the ether-based oxygenates, and may theoretically require 100 to 1,000 times greater airflow. In practice, air sparging may not be feasible if high enough airflow rates cannot be achieved without causing unwanted subsurface fracturing or contaminant mobilization. However, the biodegradation potential of both ether- and alcohol-based oxygenates will also influence system design and may reduce the airflow and time required for remediation.

In addition to the oxygenate-specific factors described above, additional variables may also affect the performance and cost of an air sparging system. These factors include the concentration, mass, and distribution of contaminants in the groundwater; subsurface geology and hydrogeology; cleanup goals; and requirements for site cleanup. For example, heterogeneity within the subsurface may result in preferential pathways that prevent injected air from contacting contaminated areas. These factors affect the number and spacing of air sparging wells, flow rates, and the length of time required for treatment, which typically will be determined during pilot testing. Air sparging also has potential to cause a lateral spread of dissolved or separate phase contaminant plumes. For example, in formations with laterally-oriented clays interbedded with sand, there is a possibility of spreading the contamination when using air sparging.

4.1.8 Conclusions

Based on the information available from the air sparging MtBE treatment profiles, and other information contained in the reference documents reviewed in preparation of this report, the following conclusions may be made regarding the use of air sparging to remediate sites contaminated with MtBE and other oxygenates:

Data from Air Sparging MtBE Treatment Profiles

- Widely used to remediate groundwater contaminated with MtBE – it was employed at 123 of 323 (38%) of projects in the dataset
- Most often used alone or in conjunction with SVE (71% of air sparging profiles in dataset); to a lesser extent has been employed with pump-and-treat or other technologies
- Employed to remediate MtBE in groundwater from concentrations greater than 1,000,000 µg/L to concentrations of less than 50 µg/L and has achieved MtBE concentration reductions greater than 99 percent
- Median project duration for different types of air sparging projects (including air sparging alone or in conjunction with SVE) ranged from 1 to 5 years
- Median reported total cost was approximately $250,000, with most projects having a total cost between $100,000 and $350,000

Treatability of MtBE and Other Oxygenates Using Air Sparging

- Increased airflow (compared to a system employed to treat only BTEX) is required to physically strip common oxygenates using air sparging; based on their Henry's Law Constants; ether-based oxygenates would require up to 10 times greater airflow and alcohol-based oxygenates would require 100 to 1,000 times greater airflow than the airflow required to physically strip the same mass of BTEX components
- Air sparging often will promote further removal of oxygenates through biodegradation mechanisms (Refer to Section 4.4 – Bioremediation for more information)
- The varied treatability of oxygenates in extracted vapors using off gas treatment technologies is an important design consideration if SVE is employed (Refer to Section 4.2 – Soil Vapor Extraction for more information)

Other Potential Advantages of Applying Air Sparging (EPA, 1995; FRTR, 2002)

- Generally considered to be easy to construct, operate, and maintain
- Configurations can be designed to cause minimal disturbance to site operations
- In some cases, such as areas of lower contaminant concentrations or in remote locations, contaminants stripped from the groundwater may be allowed to attenuate naturally in the vadose zone

Other Potential Limitations to Applying Air Sparging (EPA, 1995; FRTR, 2002)

- Often contaminants stripped from the groundwater must be extracted and treated aboveground using SVE
- High airflow rates may result in unintended fracturing leading to non-uniform flow or short-circuiting of injected air in the subsurface, or may result in unintended mobilization of contaminants as non-aqueous phase liquids (NAPL), dissolved in groundwater, or in soil gas
- Has limited applicability at sites with confined aquifers and stratified layers; soil heterogeneities may limit effectiveness
- Has potential to cause a lateral spread of dissolved or separate phase contaminant plumes

4.1.9 Example Projects

Air Sparging at Exxon and Mobil Service Stations, Smithtown, NY

A full-scale cleanup is being performed using air sparging, SVE, and groundwater pump-and-treat to prevent further off-site migration of MtBE, TBA, and BTEX in groundwater originating from two service stations in Smithtown, New York. The lithology of the site consists of fine to course grained sands with varying amounts of silt and fine gravel. At the Exxon service station, a 300-scfm air sparging system in conjunction with SVE was used to replace pump-and-treat remediation. Operation of the air sparging system began in April 2001, and was continuing to operate at the time when the profile for the project was updated (June 2003). Initial MtBE concentrations were 15,600 µg/L and initial TBA concentrations were 365 µg/L. The cleanup goal for MtBE is 1,000 µg/L; progress toward meeting the cleanup goal was not reported (EPA, 2003).

Air Sparging at Eaddy Brothers Service Station, Hemingway, SC

A full-scale cleanup is being performed using air sparging and SVE to treat MtBE and other contaminants at a service station in Hemingway, South Carolina. Soil at the site consists of silty clays with clayey sand lenses. The SVE system consisted of 230 ft of horizontal SVE piping installed immediately below the asphalt parking lot surface of the site. Extracted vapors were treated using a thermal oxidizer. The air sparging system, which began operating two weeks after the SVE system was activated, consisted of 10 vertical sparging wells, each installed at a depth of 26 ft with 5 ft well screens. The wells were connected to an air sparge compressor operating at 68 to 70 pounds per square inch (psi). Site specific target levels (SSTLs) for this site ranged from 5 to 80 µg/L per contaminant. As of June 2003, the maximum concentrations of MtBE and BTEX in the groundwater decreased, with the SSTLs being met for toluene, ethylbenzene, and xylenes. Maximum MtBE concentrations were reduced from more than 1,000,000 µg/L to 568 µg/L (a 99.99 % reduction), and maximum BTEX concentrations reduced to 9,690 µg/L. The cost for this application was $195,515 (EPA, 2003b).

4.2 Soil Vapor Extraction

Overview

- Application of a vacuum to soil to extract contaminated vapors
- EPA's MtBE Treatment Profiles dataset includes use during 138 projects to treat MtBE or other oxygenates (used during additional projects as a component of SVE)
- Used to reduce concentration and mass of MtBE and other oxygenates in soil that may be a source of groundwater contamination
- Subsurface air flow may promote biodegradation of contaminants

4.2.1 What is Soil Vapor Extraction?

SVE is an *in situ* technology in which VOCs such as MtBE and other oxygenates are removed with soil vapor from the vadose zone. It involves the application of a vacuum to the soil to create a negative pressure gradient that induces subsurface vapor flow toward one or more extraction points. Soil vapors are collected from the extraction points and generally are captured and then treated with one or more aboveground treatment technologies prior to being discharged to the atmosphere.

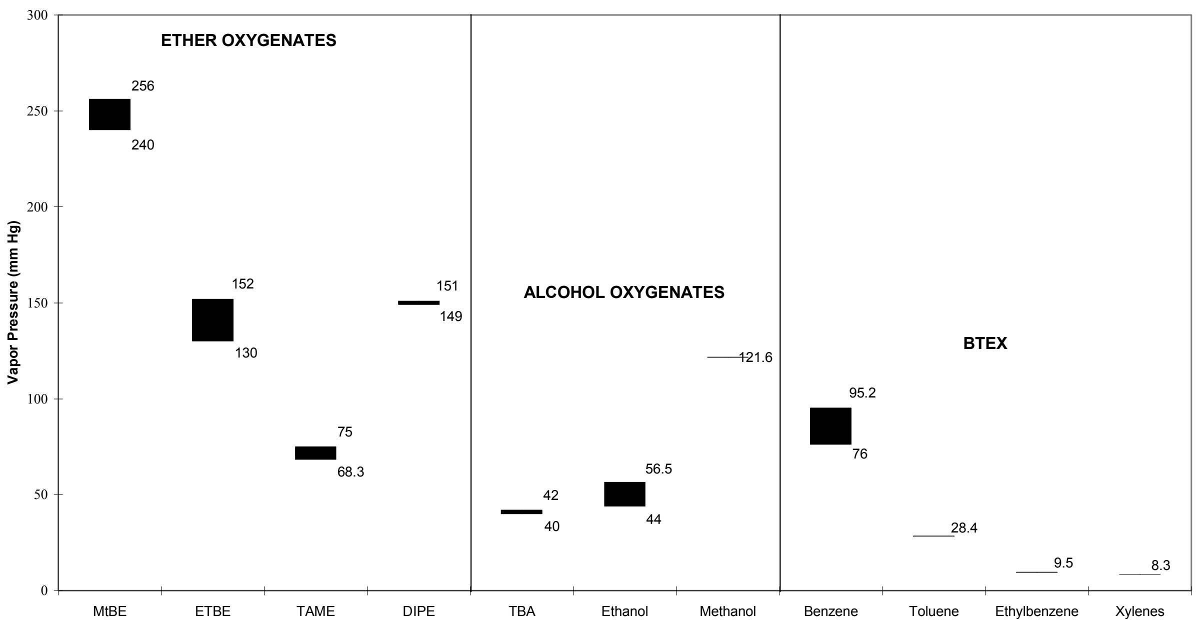
SVE is used to reduce the concentration and mass of MtBE and other oxygenates in the vadose zone, which reduces its potential to migrate as vapors into buildings or to act as a continuing source of groundwater contamination. SVE may also reduce groundwater contaminants through the enhanced evaporation of NAPL, volatilization of contaminants dissolved in pore water, and stimulation of biodegradation. SVE also is used as a component of air sparging or other systems to collect injected gases that have stripped contaminants from groundwater. This section discusses SVE used for treatment of the vadose zone only. SVE used as a component of air sparging is discussed in Section 4.1.

4.2.2 How Do the Properties of MtBE and Other Oxygenates Affect Treatment?

In an SVE system, the primary mechanism for contaminant removal from the soil to the vadose zone is the volatilization of contaminants present in the pure or adsorbed phase onto soil into the vapor phase, as the vapor phase is continually extracted. The property that shows the extent to which this transfer can take place during SVE is vapor pressure, which provides an indication of the extent to which each contaminant will partition between the liquid phase and the vapor state at equilibrium conditions. Generally, a contaminant with a greater vapor pressure more readily volatilizes than one with a lesser vapor pressure.

Figure 4.2-1 shows the vapor pressures, in units of millimeters of mercury (mm Hg), for the common fuel oxygenates as compared to BTEX. Generally, contaminants with vapor pressures greater than 10 mm Hg are considered to be amenable to treatment using SVE. As shown on the table, each of the common oxygenates have vapor pressures greater than 10 mm Hg, with ether-based oxygenates generally having greater vapor pressures than alcohol-based oxygenates. In addition, most of the common oxygenates (with the exceptions of TBA, TAME, and ethanol) have greater vapor pressures than BTEX, suggesting that they are more readily extracted using SVE than BTEX, which are commonly addressed with SVE.

Figure 4.2-1. Ranges of Vapor Pressures for Common Fuel Oxygenates



4.2.3 How is Soil Vapor Extraction Applied to Treat Oxygenates?

During SVE, contaminated soil vapors are extracted by inducing a vacuum at one or more extraction points that are typically constructed as vertical vapor extraction wells. Horizontal extraction wells or trenches have also been employed as extraction points. In general, SVE is applied at depths ranging from 10 to 50 ft bgs, but has been applied as deep as 300 ft bgs (EPA, 1995). Shallower applications typically employ some manner of a surface seal to minimize short-circuiting of the system by ambient air. Typical flow rates for extracted soil vapors range from 60 to 700 cubic feet per minute (cfm). The vacuum pressures required at the top of the vapor extraction well (wellhead vacuum) to produce the desired vapor extraction rate typically range from 3 to 100 inches of water, and vary depending on soil permeability (FRTR, 2002; EPA, 1995). The ROI of an extraction well is used to determine the number and spacing of extraction wells. The ROI is the distance from an extraction well to the point at which a vacuum can be induced to enhance volatilization and extraction of contaminants from the soil.

SVE is considered to be most effective in more homogeneous and higher permeability geologies because subsurface preferential pathways may result in short circuiting and tighter formations may minimize the radius of influence of extraction points. In general, vapor extraction points are designed and spaced to provide for a reduced pressure gradient throughout the contaminated zone. Remediation of MtBE and other oxygenates using SVE may also potentially benefit from aerobic conditions generated by subsurface air flow that may result in conditions that are amenable to *in situ* biodegradation of contaminants. At some sites, groundwater or free product extraction equipment may be incorporated into vapor extraction points. Extraction systems that incorporate the recovery of multiple phases are discussed in Section 4.3 about multi-phase extraction and separate systems to recover these other phases are discussed in Section 4.6 about groundwater pump-and-treat and Section 5.2 about product recovery.

Extracted soil vapors, containing volatilized contaminants, are routed to an aboveground treatment system prior to being discharged to the atmosphere. The types of aboveground vapor treatment technologies that have been used for treating MtBE and other fuel oxygenates include the following (Symons and Greene, 2003):

- **Adsorption** – Processes in which vapor phase contaminants are adsorbed onto a medium, such as GAC or resin, as driven by equilibrium forces

- **Thermal Treatment** – Processes in which vapor-phase contaminants are destroyed via high-temperature oxidation; primary categories of thermal treatment used to treat MtBE and other oxygenates include thermal oxidation, which employs a flame to generate the high temperatures needed to oxidize contaminants, and catalytic oxidation, which employs lower temperatures in the presence of a catalyst (typically platinum, palladium, or other metal oxide) to destroy contaminants

- **Biofilters** – Processes in which contaminants are biodegraded in a fixed-film bioreactor, typically consisting of a bed of high surface area filter media, such as GAC, that acts as a support matrix for a thin film consisting of microbes that are acclimated to the biodegradation of MtBE or other contaminants

The type of vapor treatment that is used will depend on factors such as the contaminant concentrations in the extracted vapors and the air emission discharge limitations for the site. Highly contaminated vapors at a site with stringent air emissions limitations may require a multi-step vapor treatment train, such as thermal oxidation followed by carbon adsorption. Less contaminated vapors at a site with less stringent air emissions limitation may require minimal or no vapor treatment. A significant amount of literature (some of which is listed as references at the end of this report) has been dedicated to the design of vapor treatment systems. Some of the key considerations for relevant to the treatment of MtBE and other oxygenates in extracted vapors are summarized below.

Adsorption

- Because of their equilibrium properties, MtBE and other oxygenates have a relatively low breakthrough concentration with bituminous coal-based GAC. Other, more preferentially adsorbed, contaminants in extracted vapor may reduce the capacity of GAC to remove MtBE and other oxygenates. In some cases, more absorbable contaminants may displace MtBE or other oxygenates that are already adsorbed.

- Certain types of adsorption media have been shown to preferentially adsorb certain contaminants. For example, current research shows that, in some cases, coconut shell based GAC removes MtBE better than other GAC varieties (California MtBE Research Partnership, 1999). In addition, synthetic resins have been developed to preferentially adsorb some oxygenates, such as TBA, that are less absorbable by GAC.

Thermal Treatment

- As with the treatment of other contaminants, the presence of catalyst poisons, such as metals and other inorganics, in the vapor stream can reduce the effectiveness of catalytic oxidation.

Biofilters

- Biofiltration is a newer technology that has seen less frequent use, but becoming more popular for treating soil gas contaminated with MtBE and other oxygenates; currently they are used to treat relatively low concentrations of these contaminants

One reference described the following rules of thumb for selecting vapor treatment (Fields and others, 2001):

- Thermal oxidation for VOC concentrations greater than about 2,000 parts per million by volume (ppmv)
- Catalytic oxidation for VOC concentrations between about 100 and 2,000 ppmv
- GAC treatment for VOC concentrations between about 35 and 100 ppmv
- Direct discharge for VOC concentrations less than 35 ppmv

More detailed information on the application of SVE at sites contaminated with MtBE and other oxygenates and in general is available in the following documents:

- EPA. 2001. *Development of Recommendations and Methods to Support Assessment of Soil Venting Performance and Closure*. EPA 600-R-01-070.

- Symons, Brian D., and J. Greene. 2003. *Soil Vapor Extraction, Bioventing, and Air Sparging*. In Moyer and Kostecki, Eds. 2003. MtBE Remediation Handbook. Amherst Scientific Publishers.

- U. S. Army Corps of Engineers (USACE). 1995. *USACE Engineering Manual: SVE and Bioventing*. EM 1110-1-4001.

4.2.4 What Types of Projects Involved Soil Vapor Extraction to Treat Oxygenates?

From the 323 projects listed in EPA's MtBE Treatment Profiles dataset, 138 projects were identified where MtBE was treated using soil vapor extraction. Information on the treatment of oxygenates other than MtBE during these 138 projects is limited. Two projects reported treating these other oxygenates; one project reported TBA and one reported ethanol.

Table 4.2-1 summarizes the scale and operational status for the 138 SVE projects. The data used to compile this information was current at the time the profile for each project was completed. Short summaries for two projects, *SVE at Kansas Site U6-077-231, Atwood, KS* and *SVE at Creek & Davidson Site G: Service Station, CA*, are included at the end of this section, with additional information about all 138 projects provided in Appendix A.

Table 4.2-1. General Information on 138 SVE Projects*

Technology(ies)	# of Projects	Operational Status		Scale		
		Completed	**Ongoing**	**Bench**	**Pilot**	**Full**
Soil Vapor Extraction Only	20	4	16	0	0	20
Soil Vapor Extraction with Air Sparging	74	2	72	0	0	74
Soil Vapor Extraction with Air Sparging and Pump-and-Treat	19	5	14	0	0	19
Soil Vapor Extraction with Bioremediation	1	0	1	0	0	1
Soil Vapor Extraction with *In Situ* Chemical Oxidation	2	1	1	0	0	2
Soil Vapor Extraction with Multiple Technologies	22	7	15	0	1	21
TOTAL	**138**	**19**	**119**	**0**	**1**	**137**

* Information about projects that used SVE with air sparging are discussed in Section 4.1.

As shown in Table 4.2-1, most of the 138 SVE projects were full scale (137 projects) and were ongoing (119 projects) at the time that its profile was published. In addition, most of the projects used SVE in conjunction with air sparging (74), or SVE alone (20); the remaining projects supplemented SVE treatment with bioremediation, ISCO, pump-and-treat, or multiple technologies.

The 138 SVE projects primarily used vertical wells; three projects used horizontal wells. For 23 projects for which information about the number of SVE wells was available, 20 used 2 to 8 wells per project, with an overall range of 1 to 16 wells. For the 74 projects that used air sparging with SVE, the number of SVE wells used ranged from 1 to 23 wells per project, with 30 projects in the range of 2 to 5 wells per project. Four of these 74 projects reported the type of air emission treatment used, with two reporting use of GAC, one of catalytic oxidation, and one of thermal oxidation. Eight of the SVE projects reported the types of aboveground treatment technologies that were employed to treat off gas containing MtBE and other oxygenates. For seven of these eight projects, thermal treatment was employed; six projects used catalytic oxidation and one project used thermal oxidation. One of the projects that used catalytic oxidation and one other project also used GAC adsorption to treat the SVE off gas.

4.2.5 How Has SVE Performed in Treating Oxygenates?

Several approaches have been used to evaluate SVE performance for MtBE treatment, including analyzing the changes in MtBE concentrations in soil, soil vapor, or groundwater, or estimating the mass of contaminant removed. SVE is used to reduce the mass of contaminants that may leach or otherwise migrate from the vadose zone to the groundwater. This reduced leaching rate may result in lower concentrations of contaminants in groundwater, and the performance data provided here are for MtBE concentrations in groundwater (EPA, 2001b).

The treatment performance data for 138 projects presented in Tables 4.2-2 and 4.2-3 show that SVE (either alone or in combination with other technologies) has been used to remediate MtBE in groundwater from concentrations greater than 100,000 µg/L to less than 50 µg/L and has achieved MtBE concentration reductions greater than 99 percent. The median project duration for the 19 completed sites ranged from 3 months to 5 years. Table 4.2-2 provides a summary of specific projects with performance data for one or more projects. SVE with pump-and-treat had one completed project, however, no performance data was reported and therefore was not included in the table below.

Table 4.2-2. Performance Summary for 19 Completed SVE Projects

Technology(ies)	# of Projects	Initial MtBE Concentration [1] (µg/L)			Final MtBE Concentration [1] (µg/L)			Median Project Duration (months)
		Minimum	Median	Maximum	Minimum	Median	Maximum	
Soil Vapor Extraction Only	4	48	6,900	8,900	21	1,800	3,200	24
Soil Vapor Extraction with Air Sparging	2	99	218	337	NR			57
Soil Vapor Extraction with Air Sparging and Pump-and-Treat	5	5	203	2,600	2	3	5	22
Soil Vapor Extraction with *In Situ* Chemical Oxidation	1	17,000			31			9
Soil Vapor Extraction with Multiple Technologies	7	4,151	10,800	44,400	NR			12

Notes:

NR Information not provided

[1] Treatment performance data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website, as shown in cluin.org/products/mtbe, and summarized in Appendix A. Appendix A shows the specific sites that are summarized here, along with technology design, operation, and performance data for each of the projects.

[2] Performance data are shown in terms of changes in concentration of MtBE in the groundwater, as provided in the reference materials and from the project contacts, except as noted. MtBE concentrations prior to beginning treatment (shown as "initial concentration") and after treatment was completed (shown as "final concentration") are provided. For projects where more than one technology was used, performance data are presented under each of the technologies used for the project.

Table 4.2-3. Performance Summary for 119 Ongoing SVE Projects

MtBE Concentration Range	# of Projects Reporting Initial MtBE Concentrations	# of Projects with Last Reported MtBE Concentrations
Greater than 100,000 µg/L	7	1
Greater than or equal to 10,000 µg/L but less than 100,000 µg/L	18	4
Greater than or equal to 1,000 µg/L but less than 10,000 µg/L	26	10
Greater than or equal to 100 µg/L but less than 1,000 µg/L	29	21
Greater than or equal to 50 µg/L but less than 100 µg/L	6	7
Less than 50 µg/L	20	22

4.2.6 What Costs Have Been Associated with Using SVE in Treating MtBE?

Project cost data were reported for 24 of the 138 SVE projects in the dataset; these include data for both ongoing and completed projects. In most cases, the components that make up the project costs were not reported. However, it is likely that these incorporate different components, such as treatment, monitoring, design, oversight, and health & safety. Twenty two of these projects reported were ongoing; therefore costs represent either a partial actual cost as of the time that the report was made or an estimated total project cost.

The median reported total cost for all SVE projects was approximately $206,000, with most projects having a total cost between $100,000 and $400,000.

The unit cost of SVE was reported in one literature source as ranging from $10 to $40 per cubic yard of soil treated. This source identified the cost of SVE as generally better than average among the costs for remediation technologies for treatment of contaminated soil (FRTR, 2002).

In another source, the unit cost of SVE ranged from $60 to nearly $350 per cubic yard of soil for projects treating less than 10,000 cubic yards of soil, to less than $5 per cubic yards for projects treating more than 10,000 cubic yards of soil. This source also identified the unit cost as ranging from $300 to more than $10,000 per pound of contaminant removed for projects where up to 3,000 pounds of contaminant mass were removed, to less than $15 per pound removed for projects where larger quantities were removed (EPA, 2001c). These unit cost ranges represent treatment costs for use of SVE in general, and are not specific to its use for treatment of MtBE.

4.2.7 What Factors May Affect the Performance and Cost of Oxygenate Treatment using SVE?

Key factors that affect the performance and cost of a SVE system include: the concentration, mass, and distribution of contaminants in the soil; geology and heterogeneity of the subsurface; cleanup goals; and requirements for discharging emissions to the atmosphere. These factors affect the number of vapor extraction wells, vacuum level required, type of off-gas treatment, and length of time required for treatment (FRTR, 2002).

4.2.8 Conclusions

Based on the information available from the SVE project MtBE treatment profiles and other information contained in the reference documents reviewed in preparation of this report, the following conclusions were identified regarding the use of SVE to remediate sites contaminated with MtBE and other oxygenates.

Data from SVE MtBE Treatment Profiles

- Has been used to remediate soil and groundwater contaminated with MtBE – it was employed at 138 of 323 (38%) of projects in the dataset; of these, SVE was used at 74 projects in conjunction with air sparging
- For projects without air sparging, has been used to remediate MtBE in groundwater from concentrations greater than 100,000 µg/L to less than 50 µg/L and has achieved MtBE concentration reductions greater than 99 percent
- Median project duration for different categories of projects (for example, SVE alone, SVE with pump-and-treat, etc.) ranged from 3 months to 5 years
- Median reported total cost was approximately $206,000, with most projects having a total cost between $100,000 and $400,000

Treatability of MtBE and Other Oxygenates Using SVE

- All of the common oxygenates have vapor pressures that are greater than 10 mm Hg and are amenable to treatment using SVE, with ether-based oxygenates generally having greater vapor pressures than alcohol-based oxygenates
- GAC adsorption may be less effective than other thermal treatment in removing alcohol-based oxygenates from SVE off gas

Other Potential Advantages of Applying SVE (EPA, 1995; FRTR, 2002)

- Removal of MtBE from soil generally is considered to be more cost-effective than removal of MtBE that has dissolved in the groundwater (EPA, 1995; FRTR, 2002).
- Reduces the potential for MtBE to migrate as vapors into buildings or leach to the groundwater
- Is relatively low cost compared with other remediation technologies
- Causes minimal disturbance to site operations

Other Potential Limitations to Applying SVE (EPA, 1995; FRTR, 2002)

- Low soil permeability may limit vapor movement through the soil, reducing SVE effectiveness
- At heterogeneous sites, contaminants may be difficult to extract from low permeability layers (soil vapors may be collected mainly from higher permeability layers, while contaminants may be present in lower permeability layers)
- Shallow depths to groundwater or fluctuations in the groundwater table can cause upwelling and interference with airflow
- May not be capable of reaching very stringent soil cleanup levels (soil concentrations may reach an asymptotic level that is higher than the cleanup level)

4.2.9 Example Projects

SVE at Kansas Site U6-077-231, Atwood, KS

A full scale cleanup was performed using SVE to treat MtBE from a UST site in Atwood, Kansas. Soil at the site consists of 1 to 18 ft of silt and clay overlying 18 to 50 ft of sand and gravel. The SVE system consisted of 8 vapor extraction wells, installed to a depth of 12 ft bgs. Operation of the SVE system began in February 1994 and the system is currently operational. As of June 2003, the concentration of MtBE in the groundwater has been reduced from 480 µg/L to 93 µg/L (an 80% reduction). The most recent cost data available depicts a total remediation cost of $298,040 (EPA. 2002a).

SVE at Creek & Davidson Site G: Service Station, CA

A full-scale cleanup was performed using SVE to treat MtBE and benzene from a UST leak at a service station in California. Soil at the site consists of 10 ft of clay overlying sand and gravel. The SVE system consisted of 5 vapor extraction wells and a 700 cfm vacuum system. Thermal oxidation was used for off-gas treatment. After 2.2 years of SVE operation, the concentration of MtBE in the groundwater (measured in 11 monitoring wells) was reduced from as high as 8,900 µg/L to 21 µg/L and the concentration of benzene was reduced from 670 µg/L to 0.5 µg/L (both more than 99% reductions). The thermal oxidizer destroyed greater than 95% of the VOCs in the off gases, and remediation at the site is reported to be complete. As of June 2003, the cost data available depicts a total remediation cost $140,000 (EPA. 2002a).

4.3 Multi-Phase Extraction

Overview

- Uses a combination of SVE and groundwater pump-and-treat to extract MtBE in soil vapor and groundwater, simultaneously
- EPA's MtBE Treatment Profiles dataset included use at 13 sites to treat MtBE
- Is most applicable to fine-grained formations in the fine sand to silty sand range

4.3.1 What is Multi-Phase Extraction?

MPE is a generic term for technologies that extract VOCs such as MtBE and other fuel oxygenates from the subsurface in soil vapor and groundwater, simultaneously. In addition, it can be used to remove free product or other NAPLs. MPE is referred to by several other names in the technical literature. Examples of terms referring to MPE and its configurations are dual-phase extraction (DPE), two-phase extraction (TPE), and vapor extraction/groundwater extraction (VE/GE). In general, all of these configurations couple SVE with groundwater (and in some cases NAPL) extraction and employ some form of aboveground water and vapor treatment technologies (EPA, 1999a; FRTR, 2002). Groundwater pump-and-treat and aboveground water treatment technologies are discussed in more detail in Section 4.6 and SVE and aboveground vapor treatment are discussed in more detail in Section 4.2.

4.3.2 How Do the Properties of MtBE and Other Oxygenates Affect Treatment?

The primary removal mechanisms for MPE are volatilization with subsequent air advection for the vapor phase and dissolution and aqueous advection in groundwater. Vapor pressure, solubility, and organic/water partition coefficient are the primary properties of MtBE and other oxygenates that correspond to these removal mechanisms. In general, contaminants with higher solubility and vapor pressure and lower partition coefficients, such as fuel oxygenates, are more appropriate for removal using MPE than BTEX. As shown on Table 4.3-1, the properties of both ether- and alcohol-based oxygenates suggest that they may be more favorably removed from the subsurface by the vapor and groundwater extraction components of MPE than BTEX constituents. One exception to this generalization is that certain alcohol-based oxygenates, specifically TBA and ethanol, may be less readily removed in the vapor phase because of their relatively low vapor pressures.

MPE provides several advantages when compared with use of SVE or pump-and-treat alone. MPE provides for an increase in groundwater recovery rates, an increase in radius of influence in individual groundwater recovery wells, and recovery of shallow free product. By depressing the groundwater table in the vicinity of the extraction wells, MPE provides for remediation of the capillary fringe and smear zone, and remediation of volatile, residual contaminants located above and below the water table (EPA, 1999a).

However, while the contaminant properties are important considerations in the selection and design of an MPE system for a given site, the applicability of MPE is more dependent on media properties, primarily hydraulic conductivity (K), transmissivity, depth to water table, and soil moisture (EPA, 1999a).

Table 4.3-1. Contaminant Properties Relevant to MPE

Contaminant Category	Solubility into H_2O from Gasoline Range (mg/L)	Vapor Pressure Range (mm Hg)	Partition Coefficient (log l/kg)
BTEX Constituents	3 – 100	8 – 95	1.5 – 3.2
Ether-Based Oxygenates (such as MtBE)	750 – 5,500	68 – 250	1.0 – 2.2
Alcohol-Based Oxygenates (such as TBA)	> 25,000	40 – 120	0.2 – 1.6

Source: Based on information in Table 2-2.

4.3.3 How is MPE Applied to Treat Oxygenates?

MPE can be implemented in a variety of configurations, including single pump, two pump, and bioslurping. In the single pump configuration, a single drop tube is employed to extract both liquid and vapor from a single well. The vacuum and liquid suction lift is achieved by one vacuum pump (liquid-ring pumps, jet pumps, and blowers are typical). In the two-pump configuration, a submersible pump is used for groundwater recovery in conjunction with a separate vacuum applied at the sealed wellhead. In this configuration, liquid and vapor streams are separate from one another. Depending on application, two-pump systems can use electric or pneumatic submersible pumps for groundwater recovery and liquid ring pumps or blowers to induce vacuum. Applications that recover free product or LNAPL typically use pneumatic submersible pumps for liquid recovery. Bioslurping uses the same configuration as for a single pump system, however the drop tube is set at, or just below, the liquid-air interface. The extraction point alternates from recovering liquid to air, emanating a slurping sound. This configuration has been effective in free product recovery, and also enhances *in situ* aerobic bioremediation, due to the increased airflow.

In some configurations, the vacuum used in MPE increases the effective drawdown of groundwater (i.e., increase or lower the depth to groundwater table) locally near the pumped well. This has the affect of increasing exposed soil in the saturated zone and the removal of volatile contaminants located above and below the original water table.

Extracted vapors and liquids commonly are treated aboveground. The types of technologies used for aboveground treatment are similar to those used for SVE and groundwater pump-and-treat, respectively, and are discussed further under those technologies.

More detailed information relevant to the application of MPE at sites in general or contaminated with MtBE and other oxygenates is available in the following documents:

- U.S. Army Corps of Engineers. 1999. Engineering and Design: Multi-Phase Extraction (EM 1110-1-4010). June 1. http://www.usace.army.mil/inet/usace-docs/eng-manuals/em1110-1-4010/
- U.S. Environmental Protection Agency. 1999. Multi-Phase Extraction: State of the Practice. Office of Solid Waste and Emergency Response. June. http://cluin.org/download/remed/mpe2.pdf
- U.S. Environmental Protection Agency. 1997. *Presumptive Remedy: Supplemental Bulletin, Multi-Phase Extraction Technology for VOCs in Soil and Groundwater*. Office of Solid Waste and Emergency Response. April. http://clu-in.org/download/toolkit/finalapr.pdf

4.3.4 What Types of Projects Involve MPE for Treating Oxygenates?

From the 323 projects in EPA's MtBE Treatment Profiles dataset, 13 projects were identified where MtBE was treated using MPE. Information on the treatment of other oxygenates during these 13 projects is limited; no projects reported treating other oxygenates. Table 4.3-2 summarizes the scale and operational status for the 13 MPE projects. The data used to compile this information was current at the time the profile for each project was completed. Short summaries for two projects, *MPE at Service Station A, MD*, and *MPE at Sparks Solvent/Fuel Site, Sparks, NV*, are included at the end of this section, with additional information about all 13 projects provided in Appendix A.

Table 4.3-2. General Information on 13 MPE Projects

Technology(ies)	# of Projects	Operational Status		Scale		
		Completed	Ongoing	Bench	Pilot	Full
Multi-Phase Extraction Only	9	3	6	0	4	5
Multi-Phase Extraction with Air Sparging	2	1	1	0	0	2
Multiple Phase Extraction with *In situ* Chemical Oxidation	2	0	2	0	0	2
TOTAL	**13**	**4**	**9**	**0**	**4**	**9**

As shown in Table 4.3-2, most of the 13 MPE projects were full-scale (9 projects) and were on-going (9 projects) at the time that its profile was published. Most of the projects (9) used multi-phase extraction only; the remaining 4 projects supplemented MPE with air sparging (2 projects) and ISCO (2 projects).

Five of the projects (4 pilot scale and 1 full scale) used the Bubblex system, a patented method that simultaneously extracts vapor and water using a high vacuum. One full-scale project used a VE/GE system (used at 8 sites), and 1 full-scale project used total fluid extraction with advanced oxidation technology. The VE/GE systems used 4 to 17 VE wells, with average airflow rates ranging from 4.6 to 18.5 scfm, and 2 to 8 GE wells, with pumping rates ranging from 0.11 to 0.67 gpm.

As another example, a site in Fountain Valley, CA had an air sparge/SVE system installed which appeared to remediating a BTEX plume with the exception of one recalcitrant area. However, an MTBE/TBA plume developed which did not appear to be affected by the operation of the air sparge/SVE system. MTBE was reduced but the TBA concentration was found to be increasing. After conducting feasibility tests, a dual-phase extraction (MPE) system to remove and treat ground is being installed (O'Connell, 2004).

4.3.5 How Has MPE Performed in Treating Oxygenates?

For the 13 projects identified from 323 MtBE treatment profiles, MPE treated MtBE with concentrations as high as 100,000 µg/L (JFK International Airport, Jamaica City, NY) and achieved as low as 50 µg/L in groundwater after treatment. None of the 13 projects listed TBA as a contaminant. Therefore, this section only highlights performance for MtBE.

Tables 4.3-3 and 4.3-4 summarize performance data for 3 completed and 7 ongoing MPE projects. Because the dataset included relatively few completed projects with performance data, Table 4.3-3 provides a summary of specific projects instead of a summary of minimum, median, and maximum concentrations. The reason for the increase in the MtBE concentration at the Tahoe Boat Company, CA site was not specified.

Table 4.3-3. Completed MPE Projects - Performance Summary for 3 Projects

Technology(ies)	Site Name and Location	Scale	Initial MtBE Concentration [1] (µg/L)	Final MtBE Concentration [1] (µg/L)	Median Project Duration (months)
Multi-Phase Extraction Only	Site CA – X, Lawndale, CA	Pilot	11	NR	NR
Multi-Phase Extraction Only	Eight Service Stations MD – A, MD	Full	6,140	791	NR
Multi-Phase Extraction with Air Sparging	Tahoe Boat Company, Lake Tahoe, CA	Full	55	79	45

Notes:

NR Information not provided

[1] Treatment performance data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website, as shown in cluin.org/products/mtbe, and summarized in Appendix A. Appendix A shows the specific sites that are summarized here, along with technology design, operation, and performance data for each of the projects.

[2] Performance data are shown in terms of changes in concentration of MtBE in the groundwater, as provided in the reference materials and from the project contacts, except as noted. MtBE concentrations prior to beginning treatment (shown as “initial concentration”) and after treatment was completed (shown as “final concentration”) are provided. For projects where more than one technology was used, performance data are presented under each of the technologies used for the project.

Table 4.3-4. Ongoing MPE Projects - Performance Summary for 7 Sites

MtBE Concentration Range	# of Projects Reporting Initial MtBE Concentrations	# of Projects with Last Reported MtBE Concentrations
Greater than or equal to 10,000 µg/L but less than 100,000 µg/L	1	0
Greater than or equal to 1,000 µg/L but less than 10,000 µg/L	1	2
Greater than or equal to 100 µg/L but less than 1,000 µg/L	2	0
Greater than or equal to 50 µg/L but less than 100 µg/L	0	1
Less than 50 µg/L	0	1

Note:

Performance data were not available for some sites

4.3.6 What Costs Have Been Associated with Using MPE in Treating MtBE?

The total project cost was reported for 2 of the 13 MPE projects identified above. The completed Kings Beach Swiss Mart, CA project, which employed MPE alone, reported a total project cost of $130,000 and the completed Tahoe Boat Company, CA project, which employed MPE with air sparging, reported a total project cost of $383,000. Both of these total costs were the amounts reported by the state cleanup fund. Because the area, volume, or mass treated was not available for this project, a unit cost was not calculated.

Little additional information was identified in the literature about the costs of using MPE for the treatment of MtBE and other oxygenates, or for other contaminants. The cost per volume of subsurface treated (identified as cubic yards of subsurface) was reported in one literature source as ranging from $36 to $170 per cubic yard for sites contaminated with chlorinated solvents (EPA, 1999a). The cost of MPE generally is considered to be average, among the costs for remediation technologies, for treatment of contaminated groundwater (FRTR, 2002). However, project costs will likely be driven primarily by the aboveground treatment required. The cost of aboveground water treatment technologies is discussed in Section 4.6; the cost for aboveground vapor treatment is discussed in Section 4.2.

4.3.7 What Factors May Affect the Performance and Cost of Oxygenate Treatment using MPE?

When MtBE or other oxygenates are present and must be remediated at a site, MPE, either alone or in combination with other technologies, may be a suitable remediation approach. MPE affects mass removal by volatilization, dissolution, and advective transport. In general, if both SVE and groundwater pump-and-treat are potentially applicable technologies, then MPE may be considered as a remedial alternative. The performance of MPE is governed, primarily, by media properties and, to a lesser extent, by contaminant properties. MPE is most applicable to fine-grained formations in the fine sand to silty sand range ($K = 10^{-3}$ to 10^{-5} centimeters per second) with low transmissivity (less than 200 gallons per day per foot).

A typical result of conventional pumping in low conductivity and transmissivity formations is increased, and sometimes rapid, drawdown with steep gradients, with corresponding low recovery rates. This condition limits the influence of the conventional pumping well. MPE overcomes this limiting factor with the application of a vacuum. The vacuum enhancement of MPE also can overcome the capillary forces that can trap contaminants within the capillary zone. This allows better recovery of LNAPL, which tends to accumulate in the capillary zone at the air-water interface.

In addition to the technology-specific factors described above, additional factors may also affect the performance and cost of any MPE system. These factors include:

- The concentration, mass, and distribution of contaminants in the soil and groundwater
- Geology, hydrogeology, and heterogeneity of the subsurface; cleanup goals
- Requirements for air emissions and water discharges

These factors affect the number and type of extraction wells, vacuum level, pumping rate, type of aboveground water and off-gas treatments, and length of time required for treatment (FRTR, 2002). More information about the factors that influence the performance and cost of air sparging systems in general is available in the references listed in this report.

4.3.8 Conclusions

Based on the information available from the MPE project MtBE treatment profiles and other information contained in the reference documents reviewed in preparation of this report, the following conclusions were identified regarding the use of MPE to remediate sites contaminated with MtBE and other oxygenates.

Data from MPE MtBE Treatment Profiles

- Has been used to remediate groundwater contaminated with MtBE, but less frequently than some other technologies, such as air sparging and bioremediation – it was employed at 13 of the 323 (4%) of the projects in the dataset
- Most often used without in situ technologies (70% of projects in dataset); to a lesser extent has been employed in conjunction with air sparging or ISCO
- Has been used to remediate MtBE in groundwater from concentrations greater than 100,000 μg/L to less than 50 μg/L and has achieved MtBE concentration reductions greater than 99 percent
- Cost information is limited – total costs for two project in dataset were $130,000 and $383,000

Treatability of MtBE and Other Oxygenates Using MPE

- While the contaminant properties are important considerations in the selection and design of an MPE system for a given site, the applicability of MPE is more dependent on media properties, primarily hydraulic conductivity and transmissivity (EPA, 1999a).

Other Potential Advantages of Applying MPE (EPA, 1999a)

- Has potential for increase in groundwater recovery rates, compared to conventional pumping practices in equivalent settings
- Has potential for increase in radius of influence of individual groundwater recovery wells
- Has potential for recovery of free product or other LNAPL
- Has potential for remediation of the capillary fringe and smear zone
- Simultaneous remediation of soil vapors and groundwater
- Effective on lower permeability soil sites

Other Potential Limitations of Applying MPE (EPA, 1999a)

- Potentially greater aboveground treatment requirements as a result of NAPL emulsions and VOC-laden vapors
- Initial start-up methods and adjustment period may be longer, compared to conventional practices
- Potentially higher capital costs compared to conventional pumping approaches
- Depth limitations to some MPE configurations

4.3.9 Example Projects

MPE at a Service Station MD-A, MD

At a service station in Maryland, MPE was conducted using a VE/GE system that consisted of 10 VE wells and 6 GE wells. The sites were located on coastal plain, and the soil consisted of sandy silts and clays. The average flow rates were 9.8 scfm in the VE wells and 0.24 gpm for the GE wells. The concentration of MtBE in groundwater was reduced from 27,027 μg/L to 32 μg/L over 3.5 years of system operation. The cleanup was reported as completed, however a cleanup goal was not provided (EPA, 2000c).

MPE at Sparks Solvent/Fuel Site, Sparks NV

Since 1995, the Sparks Solvent/Fuel Site located in Sparks, Nevada, a remediation system consisting of MPE, air sparging, and SVE has been operational. The treatment system consists of 29 MPE wells, an oil-water separator, and a fluidized bed bioreactor, with an influent flow rate of 370 gpm and a retention time of 8 minutes. Vapors are sent through a condenser, followed by a thermal oxidizer, before release to the atmosphere. Condensate is sent back through the oil-water separator. Performance data, available for the first 650 days of site operation, showed a reduction in MtBE concentration across the bioreactor from 2,400 to 55 µg/L. No data was provided for reduction of MtBE concentrations in the aquifer (EPA, 2000b).

4.4 *In Situ* Bioremediation

Overview

- Enhances the mechanisms that biologically degrade MtBE and other oxygenates in contaminated soil and groundwater
- EPA's MtBE Treatment Profiles dataset includes use at 73 sites to treat MtBE; 12 of these sites also reported treating TBA
- Typically used to treat residual soil and groundwater contamination after contaminant source has been removed

4.4.1 What is Bioremediation?

Bioremediation is a process by which microorganisms, fungi, and plants metabolize pollutant chemicals. It has been used to treat oxygenates in soil and groundwater both *in situ* and *ex situ*. Generally, an engineered bioremediation system stimulates the biodegradation of contaminants through the introduction of electron acceptors (typically oxygen), electron donors (substrates or food sources), nutrients, or microbes that are acclimated to the contaminated soil or groundwater. These amendments are either introduced to the subsurface *in situ* or are added to extracted groundwater or excavated soil. A description of the various types of amendments is provided below (Wilson, 2003c).

Amendments

- **Electron Acceptors** – Oxygen is the most common electron acceptor used to promote biodegradation and is added in different ways including: in sparged air, through injection of a solid or liquid that generates oxygen, or through *in situ* electrochemical generation. Other electron acceptors, including nitrate, sulfate, and iron (III) compounds, may be added to support anaerobic biodegradation.
- **Electron Donors** – In direct biodegradation pathways, the contaminant acts as the electron donor or substrate. However, during cometabolic degradation, a different electron donor is metabolized, resulting in the consequential oxidation of the contaminant. In some contaminated plumes, other electron donors, such as other constituents of gasoline, may also be present. In cases where they are not, and cometabolic degradation pathways are desired, electron donors may be added.
- **Nutrients** – Nutrients, such as nitrogen and phosphorus and other trace elements, are necessary for cell growth because they are key biological building blocks. Addition of nutrients as a supplement helps ensure that concentrations of nutrients do not become a limiting factor for bioremediation.
- **Bioaugmentation** – involves the addition of supplemental microbes to the subsurface where organisms able to degrade specific contaminants are deficient. Microbes may be grown from populations already present at a site or "seeded" from cultures grown in aboveground reactors or available commercially as cultivated strains of bacteria known to degrade specific contaminants. The application of bioaugmentation technology is highly site-specific and dependent on the microbial ecology and physiology of the subsurface (EPA, 1998b).

This section focuses on engineered *in situ* remediation technologies that use microorganisms to biodegrade pollutant chemicals. *In situ* bioremediation technologies are configured to either directly inject supplements into the contaminated media; to place the supplements in the pathway of groundwater flow; or to extract contaminated groundwater, amend it with supplements, and recirculate the amended groundwater through the contaminated zone (further information about groundwater extraction is provided in Section 4.6 about pump-and-treat). EPA policy regarding injection of supplements is discussed in Section 3.4. Some of the key considerations for various types of engineered *in situ* remediation systems are summarized below (EPA, 1998b). A discussion of *ex situ* applications of bioremediation, which focuses on biological treatment of extracted groundwater, is included in Section 4.7 about treatment of extracted groundwater.

Engineered Systems

- **Direct Injection Wells/Trenches** – In a direct injection system, degradation is enhanced through the addition of microbes, nutrients, electron acceptors, or electron donors directly into the aquifer at injection points or directly into the soil. Direct injection technologies include those that employ injection wells or trenches through which supplements are introduced. Some common direct injection technologies use chemical or electrochemical means to increase the level of oxygen in the groundwater, or inject microorganisms that are specifically conditioned to degrading the contaminants of concern. The natural flow of the groundwater generally is not impeded, but is monitored to determine that the degradation of the contaminants and their daughter products is completed within an acceptable distance from the source.
- **Recirculation Systems** – A recirculation system extracts contaminated groundwater from the site, adds to or amends the extracted water ex situ, and reinjects the “activated” water to the subsurface, generally upgradient of the contaminated zone. As an alternative, extraction and injection are performed at different elevations in a single well, creating vertical circulation. A groundwater recirculation configuration may be used to provide containment of a plume or to allow the addition of amendments in a more controlled environment.
- **Permeable Reactive Barriers** – The placement of supplements in the pathway of groundwater flow constitutes a PRB, sometimes referred to as a treatment zone or “bio-barrier”. With a PRB approach, an active bioremediation zone is created by such methods as backfilling a trench with nutrient-, oxidant-, or reductant-rich materials, or by creating a curtain of active bioremediation zone through direct injection or groundwater recirculation at the toe of a plume. PRBs contain a contaminant plume by treating only groundwater that passes through it.

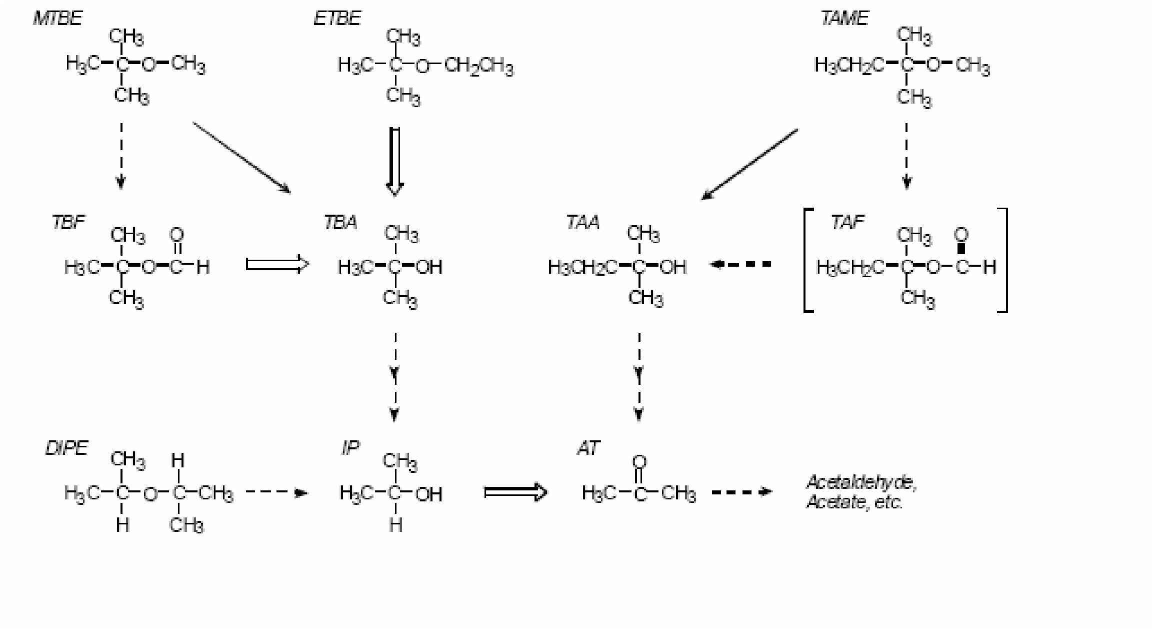
The design and configuration of *in situ* bioremediation systems varies widely based on site-specific conditions. A treatability study or pilot-scale testing is often performed to determine the type and amount of amendments required to create and maintain the conditions optimal for biodegradation as well as to select the type of engineered system that is most suitable to introduce the amendments to the subsurface (EPA, 2000a).

4.4.2 How Do the Properties of MtBE and Other Oxygenates Affect Treatment?

Early studies on MtBE contamination of groundwater concluded that the compound was either non-biodegradable or very resistant to biodegradation. However, more recent research has shown that MtBE can be degraded both aerobically and anaerobically, although anaerobic intrinsic degradation rates are relatively slow. The research has found that there are naturally occurring microbes capable of using MtBE as their sole carbon and energy source. Such microorganisms seem to be widespread, but are present natively in low numbers and take time to reach a sufficiently dense population to sustain MtBE degradation. As a result, cometabolic approaches are often considered for MtBE bioremediation, wherein an organic substrate (electron donor) that is readily degraded is added to the subsurface, resulting in the consequential oxidation of MtBE. Because the ability of microorganisms to cometabolically degrade MtBE is consistently found in strains that are predisposed to catabolize structural analogs of MtBE, suitable co-substrates include simple branched and even non-branched alkanes such as propane and butane (Wilson, 2003a; Bradley, 2001; Vance, 2003; Hyman, 2000; Steffan et al, 1997).

Although detailed comparative evaluations of the aerobic degradation rates of other fuel oxygenates have not been performed to date, the aerobic biodegradation rates of TAME, EtBE, DIPE, TBA, and TAA were observed to be of the same order of magnitude as the aerobic degradation rate of MtBE in one research study using a mixed culture (Church and Tratnyek, 2000). Together with the similarity of product chemical structure, these results suggest that the same or similar enzyme systems and pathways are responsible for the biodegradation of these oxygenates (see Figure 4.4-1 below) and that the bioremediation of fuel oxygenates other than MtBE therefore has similar constraints (EPA 2001a).

Figure 4.4-1. Proposed Degradation Pathway of MtBE and Other Oxygenates (Church and Tratnyek, 2000)



Successful field-scale applications of engineered bioremediation systems have been limited to the aerobic pathway, as opposed to the anaerobic pathway. The advantages of the aerobic pathway include:

- More energy is derived by microorganisms from the aerobic metabolism of MtBE and other fuel oxygenates; consequently, MtBE degrading cultures grow more quickly under aerobic conditions
- There are a number of aerobes that are known to use MtBE as a sole carbon and energy source; anaerobic pathways and the types of microorganisms involved are less well documented
- Where the terminal electron acceptor is not present initially in sufficient quantity, addition of oxygen for aerobic bioremediation can be as simple as bubbling air into the aquifer; addition of electron acceptors for anaerobic bioremediation is more complex and can foster concerns regarding the toxicity and fate of the added material
- Laboratory studies have provided inconsistent results regarding the degree to which MtBE is biodegraded anaerobically to end products and the extent to which other oxygenates are biodegraded under anaerobic conditions

However, the many pathways by which MtBE and other oxygenates may be biodegraded anaerobically have been the subject of recent research and ongoing studies. Table 4.4-1 highlights the various electron acceptors that are used in anaerobic bioremediation studies and contrasts the products of complete anaerobic degradation with those for aerobic metabolism.

Table 4.4-1. MtBE Biodegradation Mechanisms and Products

Zone		Electron Donor	Electron Acceptor	Products of Complete Degradation
Aerobic		MtBE	O_2	CO_2 and H_2O
Anaerobic	Nitrate Reducing	MtBE	NO_3^-	N_2, NH_3, CO_2, and H_2O
	Iron Reducing	MtBE	Fe^{+3}	Fe^{+2}, CO_2, and H_2O
	Sulfate Reducing	MtBE	SO_4^{-2}	H_2S, CO_2, and H_2O
	Methanogenic	MtBE	CO_2	CH_4, CO_2, and H_2O

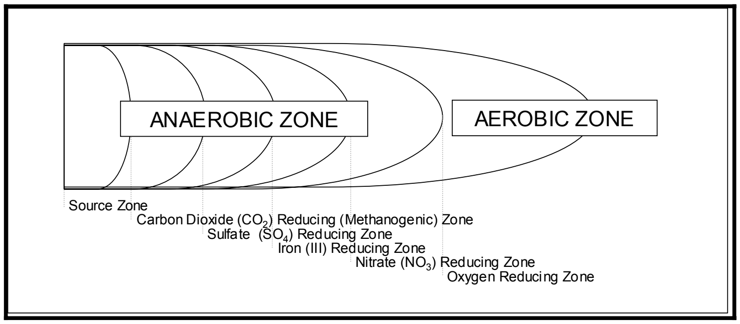
While Table 4.4-1 lists the products of complete degradation of MtBE, incomplete degradation of MtBE and other oxygenates may also occur under certain conditions. Of specific note, TBA has been shown to be a degradation intermediate that may persist under anaerobic conditions (Vance et al, 2003). In some cases, this can result in MtBE plumes having a concentration of TBA in excess of the concentration of MtBE (Wilson, 2003a). A paper published as this report went to print (Schmidt, 2004) provides further information about the role of TBA in microbial biodegradation. Therefore, application of bioremediation approaches to MtBE and other oxygenates often have considered the complete pathway to end products and the possible stall of the bioremediation process at intermediates along that pathway.

4.4.3 How is Bioremediation Applied to Treat Oxygenates?

Bioremediation is applied to MtBE and other oxygenates in systems that range in complexity from not being engineered at all (natural biodegradation) to systems that are completely engineered, including the addition of conditioned microorganisms (bioaugmentation) and of nutrients as well as co-substrates and electron acceptors (biostimulation). Further, these systems can be based on aerobic or anaerobic pathways, or a sequential combination of these pathways.

The rate at which natural biodegradation of MtBE and other oxygenates will occur at a site is affected by a number of site conditions, including groundwater chemistry, presence of other contaminants, and number of native microbes capable of degrading MtBE or other oxygenates. Whether the contaminated zone is aerobic or anaerobic (nitrate reducing, iron reducing, sulfate reducing, or methanogenic), and other chemical parameters (for example, pH, alkalinity, and inorganic content) will determine what types of microbes may be able to grow and what type of biodegradation pathway may be followed. Figure 4.4-2 depicts the oxidative zones which may be present in a plume at a petroleum-contaminated site and illustrates how each of the anaerobic and aerobic pathways listed in Table 4.4-2 may be part of the natural biodegradation process.

Figure 4.4-2. Typical Zones Downgradient of Petroleum Contaminant Source



Source: Modified from Anderson, R.T. and D.R. Lovley 1997

Multiple microbes that are capable of biodegrading oxygenates have been identified at sites contaminated with MtBE and other oxygenates. Whether such microbes are present at a specific site will affect the viability of natural biodegradation without the need for bioaugmentation. Where these microbes are present, natural biodegradation or limited biostimulation, such as air sparging to increase oxygen levels, may be effective in reducing the concentrations of MtBE and other oxygenates. However, other conditions must be conducive to support significant natural biodegradation. Typically, only those sites that have aerobic conditions in the contaminated zone because of shallow water tables and high rates of groundwater recharge have achieved significant natural biodegradation of MtBE and other oxygenates (Stocking et al., 2000).

In some cases, the presence of other contaminants, such as benzene, has been shown to facilitate the natural biodegradation of MtBE and other oxygenates through co-metabolism. However, contaminants such as BTEX also may inhibit the biodegradation of oxygenates through the depletion of electron acceptors or nutrients, or may be preferentially used because of the relatively slow growth of oxygenate-degrading microorganisms (EPA, 2001a; Deeb and Kavanaugh, 2002).

In addition, sites contaminated with alcohols such as ethanol also may inhibit the biodegradation of ether-based oxygenates such as MtBE through the depletion of electron acceptors or nutrients (da Silva, 2003).

Fully-engineered systems for the bioremediation of oxygenates typically incorporate both biostimulation and bioaugmentation to accelerate the biodegradation process. Most commonly, these systems are based on the aerobic pathway so that the biostimulation component includes the addition of oxygen, through air/oxygen sparging or addition of oxygen releasing chemicals, as well as the addition of nutrients. The addition of oxygen through one of these means can be used to make the entire contaminant zone aerobic and thereby provide more uniform conditions for accelerated biodegradation. Maintaining high oxygen levels is especially important to effective aerobic biodegradation in that oxygenate-degrading organisms have been shown in research studies to require a higher concentration of oxygen. The bioaugmentation component is achieved by adding microbial cultures that are conditioned to degrade oxygenates either by being grown on these contaminants or by culturing isolated species that have the required enzymes. Bioaugmentation is often critical to the success of an engineered bioremediation system in that microorganisms capable of degrading oxygenates may not be present natively and are slow growers (Rittman, 2003, Wilson, 2003b).

The use of anaerobic pathways may have engineering advantages under certain conditions, such as in treating oxygenate contamination in deep aquifers or source zones. Recent research and field studies have focused on the various anaerobic pathways for biodegradation of MtBE and other fuel oxygenates (Vance et al, 2003). However, the results of these studies in terms of oxygenate degradation efficiency have been variable and no single anaerobic pathway has demonstrated consistent success for degrading oxygenates to end products, even in the laboratory environment (Finneran and Lovely, 2003e). Therefore, site-specific treatability studies and pilot testing are generally performed if bioremediation using anaerobic pathways is to be considered at a site.

Engineered systems may also incorporate the addition of a co-substrate to help establish an active microbial community and thereby accelerate the biodegradation of oxygenates. Hydrocarbon gases, such as propane and butane are one type of co-substrates that has been used in field applications due to the simplicity of injecting and diffusing a hydrocarbon gas (Steffan et al, 2003). Some proprietary technologies are based on the use of specific co-substrates and strains of microbes.

4.4.4 What Types of Projects Involved Bioremediation to Treat Oxygenates?

From the 323 MtBE projects in EPA's MtBE Treatment Profiles dataset, 73 projects were identified where MtBE was treated using engineered bioremediation systems, either alone or in conjunction with another technology. Information on the treatment of other oxygenates during these 73 projects is limited, with a total of 12 of the 73 projects reporting TBA as a co-contaminant.

Table 4.4-2 summarizes the scale and operational status for the 73 bioremediation projects. These projects include only engineered bioremediation systems and exclude projects that used natural biodegradation as part of a monitored natural attenuation approach (see Section 5.3 for a discussion of monitored natural attenuation).

Table 4.4-2. General Information from 73 Engineered Bioremediation Projects

Technology(ies)	# of Projects	Operational Status		Scale		
		Completed	Ongoing	Bench	Pilot	Full
IN SITU PROJECTS						
Bioremediation Only	55	25	30	2	12	41
Bioremediation with Air Sparging	2	0	2	0	1	1
Bioremediation with Pump-and-Treat	1	0	1	0	0	1
Bioremediation with SVE	1	0	1	0	0	1
Bioremediation with Air Sparging and SVE	6	6	0	0	0	6
Bioremediation with Multiple Technologies	1	0	1	0	0	1
EX SITU PROJECTS						
Bioremediation Only	7	4	3	5	0	2
TOTAL	**73**	**35**	**38**	**7**	**13**	**53**

As shown in Table 4.4-2, 62 of the 73 bioremediation projects employed either *in situ* or *ex situ* bioremediation alone. However, 11 of the projects supplemented bioremediation treatment with air sparging, SVE, or pump-and-treat. Most of the bioremediation projects in the dataset were full scale (53 projects) and were ongoing (38 projects) at the time that its profile was published. For the 40 projects specifying the type of MtBE biodegradation mechanism employed, 37 reported using the aerobic pathway, 1 project reported using cometabolic pathways, 1 project reported using a combination of aerobic and anaerobic pathways, and 1 project reported using a combination of aerobic and cometabolic pathways. Short summaries for two of these projects, *In Situ Bioremediation at Port Hueneme - D,* *Oxnard, CA, In Situ Bioremediation at Sunoco Service Station, MA*, and *In Situ Bioremediation at South Beach Marina, Hilton Head, South Carolina,* are included at the end of this section, with additional information about all 73 projects provided in Appendix A.

4.4.5 How Has *In Situ* Bioremediation Performed in Treating Oxygenates?

Tables 4.4-3 and 4.4-4 summarize performance data for the 35 completed and 38 ongoing *in situ* bioremediation projects that reported this information. The concentration of MtBE in groundwater prior to treatment was as high as 870,000 µg/L (ongoing project at Site NY - F), and as low as 10 µg/L (Main Street Shell Conway, SC and Speedway #226, North Charleston, SC).

Table 4.4-3. Completed *In Situ* Bioremediation Projects Performance Summary for 31 Projects

Technology(ies)	# of Projects	Initial MtBE Concentration [1] (µg/L)			Final MtBE Concentration [1] (µg/L)			Median Project Duration (months)
		Minimum	Median	Maximum	Minimum	Median	Maximum	
In situ Bioremediation Only	25	5	2,800	100,000	1	35	33,000	6
In situ Bioremediation with Air Sparging and SVE	6	4,151	10,800	44,400	NR	NR	NR	12

Notes:

NR Information not provided

[1] Treatment performance data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website, as shown in cluin.org/products/mtbe, and summarized in Appendix A. Appendix A shows the specific sites that are summarized here, along with technology design, operation, and performance data for each of the projects.

[2] Performance data are shown in terms of changes in concentration of MtBE in the groundwater, as provided in the reference materials and from the project contacts, except as noted. MtBE concentrations prior to beginning treatment (shown as "initial concentration") and after treatment was completed (shown as "final concentration") are provided. For projects where more than one technology was used, performance data are presented under each of the technologies used for the project.

Table 4.4-4. Ongoing *In Situ* Bioremediation Projects Performance Summary for MtBE at 38 Sites

MtBE Concentration Range	# of Projects Reporting Initial MtBE Concentrations	# of Projects Reporting Post-treatment MtBE Concentrations
Greater than 100,000 µg/L	1	0
Greater than or equal to 10,000 µg/L but less than 100,000 µg/L	12	1
Greater than or equal to 1,000 µg/L but less than 10,000 µg/L	11	3
Greater than or equal to 100 µg/L but less than 1,000 µg/L	4	3
Greater than or equal to 50 µg/L but less than 100 µg/L	0	1
Less than 50 µg/L	5	5

The data presented in Table 4.4-3 and Table 4.4-4 shows that bioremediation (either alone or in combination with other technologies) has been employed to remediate MtBE in groundwater and soil to concentrations less than 50 µg/L and has achieved MtBE concentration reductions greater than 99 percent. The median project duration for the 20 completed sites ranged from 6 months to 1 year.

In addition to the performance data reported for MtBE, 8 of the 12 projects in the dataset that reported treating TBA using bioremediation also provided performance data. All 8 of these sites provided TBA concentration prior to bioremediation treatment (the highest initial concentration was 90,000 µg/L) and 2 provided TBA concentrations following treatment (both achieved less than 5 µg/L).

Because of the heightened interest in bioremediation of TBA, additional information was obtained about several of these sites. These data, provided in the online database, show that several sites were able to reduce the concentration of TBA, sometimes to less than its site-specific cleanup level. For example, at several sites in Texas, including Turtle Bayou Easement Area and Rural Area Disposal Area, *in situ* bioremediation was used in conjunction with other technologies such as SVE and *in situ* thermal desorption. At these sites, the concentrations of TBA were reduced to less than its cleanup goal, with concentrations after treatment ranging from 100 – 1,000 µg/L. At the Naval Base Ventura County, Port Hueneme, CA, *in situ* bioremediation was used in a biobarrier configuration, and the concentration of TBA was reduced from >1,000 to <5 µg/L (information about required cleanup levels was not provided).

4.4.6 What are the Costs of Using *In Situ* Bioremediation to Treat Oxygenates?

Project cost data were reported for 28 of the 73 bioremediation projects in the dataset; these include data for both ongoing and completed projects. In most cases, the components that make up the project costs were not reported. However, it is likely that the reported costs incorporate different components, such as treatment, monitoring, design, oversight, and health & safety. Most (21 projects) of the reported costs were for ongoing projects and represent either a partial actual cost as of the time that the report was made or an estimated total project cost.

The median reported total cost for all bioremediation projects was approximately $125,000, with most projects having a total cost between $50,000 and $350,000. The total cost for all 28 projects reporting this information ranged from $4,000 to $5,200,000 per project, depending on scale, type of engineered application, and site conditions. For example, as shown in Section 4.4.8, at the Port Hueneme site, a 500-ft wide biobarrier was constructed in a shallow sand aquifer and had an installation cost of $435,000, with first year O&M costs of $75,000. At a site in South Carolina, 3,000 gallons of a liquid microbial solution were injected through 40 monitoring and 15 injection points, for a total cost of $63,500.

Because the area, volume, or mass treated was not consistently available for the 28 bioremediation projects, no unit costs were estimated. The cost per volume of subsurface treated (identified as cubic yards of subsurface) was reported in one literature source as ranging from approximately $170 to $330 per cubic yard for *in situ* bioremediation in general. This source also reported unit costs for *ex situ* bioremediation ranging from $12 to more than $1,000 per cubic yard treated (EPA, 2001c). These results suggest that the cost for bioremediation is highly variable and depends on site-specific conditions and remedial goals. Overall, the cost of bioremediation generally is considered to be better than the average for applicable groundwater remediation technologies (FRTR, 2002).

4.4.7 What Factors May Affect the Performance and Cost of Oxygenate Treatment using *In Situ* Bioremediation?

When oxygenates are present and must be remediated at a site, bioremediation, either alone or in combination with other technologies, may be a suitable remediation approach. Although both ether- and alcohol-based oxygenates are susceptible to biodegradation, the site conditions will determine whether bioremediation is an appropriate technology for a given site. Key factors that affect the performance and cost of bioremediation include: the concentration, mass, and distribution of VOCs in the soil and groundwater; geology, moisture content, mineral content, pH, temperature, the concentrations of terminal electron receptors and nutrients, as well as the presence of appropriate microbes, in the subsurface; cleanup goals; and requirements for site cleanup. These factors affect the design of bioremediation system, the biodegradation pathways that can be employed, and the amendments that must be added to enhance bioremediation (EPA, 1995; FRTR, 2002).

Bioremediation generally is considered to be more suitable for the dissolved phase in groundwater plumes or low concentrations in soil rather than grossly contaminated source areas where free product may be present. Other technologies that incorporate free product removal, such as MPE and pump-and-treat, are generally considered more applicable to source areas. Therefore, source areas are typically treated through removal or another technology prior to application of bioremediation. Research is ongoing into the potential use of bioremediation near source areas.

Because of the above factors, the design of a bioremediation system is typically based on significant site analysis and bench- and pilot-scale testing rather than the application of packaged treatment systems. More information about the factors that influence the performance and cost of bioremediation systems is available in the references listed in this report.

4.4.8 Conclusions

Based on the information available from the bioremediation project, MtBE treatment profiles, and other information contained in the reference documents reviewed in preparation of this report, the following conclusions may be made regarding the use of bioremediation to remediate sites contaminated with MtBE and other oxygenates:

Data from Bioremediation MtBE Treatment Profiles

- Used to remediate groundwater contaminated with oxygenates – it was employed at 73 of the 323 of the projects in the dataset, primarily in the in situ mode
- Most often used alone (92% of projects in dataset); to a lesser extent has been employed in conjunction with air sparging, pump-and-treat, or SVE
- Employed to remediate MtBE in groundwater from concentrations greater than 100,000 μg/L to less than 50 μg/L and has achieved MtBE concentration reductions greater than 99 percent
- Median project duration is approximately 1 year
- Median reported total cost for all bioremediation projects in the dataset was approximately $125,000, with most projects having a total cost between $50,000 and $350,000

Treatability of Oxygenates Using Bioremediation

- Most research has focused on bioremediation of MtBE and TBA; information on biodegradation of other oxygenates is limited, but similar degradation pathways are employed for many oxygenates

- Presence of ethanol may affect the aerobic biodegradation of MtBE and lead to longer MtBE plumes. Recent research has indicated that ethanol can deplete available electron acceptors and stimulate methanogenesis.
- Effective biodegradation of MtBE and other oxygenates has been reported in a variety of applications of the aerobic pathway; results for anaerobic pathways have been confined to laboratory studies and have not been consistent
- Intermediate degradation products of MtBE and other oxygenates, such as TBA, may remain in the subsurface under natural conditions or when using anaerobic pathways
- Oxygenate-degrading microorganisms are typically very slow growing; bench- and pilot-studies may be needed to confirm the applicability of bioremediation and to select an appropriate design

Other Potential Advantages of Applying Bioremediation (EPA, 1995; EPA, 2000a)

- Application involves equipment that is widely available and relatively easy to install
- In situ systems create minimal disruption and/or disturbance to ongoing site activities
- Time required for subsurface remediation using aerobic bioremediation may be shorter than time required for pump-and-treat
- Is generally recognized as being less costly than other remedial options (for example, pump-and-treat or chemical oxidation)
- Can be combined with other technologies (for example, bioventing, soil vapor extraction) to enhance site remediation
- In many cases, does not produce waste products that require disposal

Other Potential Limitations to Applying Bioremediation (EPA, 1995; EPA, 2000a):

- Injection wells and/or infiltration galleries may become plugged by microbial growth or mineral precipitation.
- Oxygenate-degrading microorganisms are typically slow growing and may not be present natively at all sites; pilot or treatability studies may be needed to confirm the applicability of bioremediation at a specific site
- Bioremediation of source zones may take substantial time due to the presence of free product and lack of immediate bioavailability
- Difficult to implement in low-permeability aquifers (hydraulic conductivity less than 10^{-4} centimeters per second)
- Re-injection wells or infiltration galleries may require permits or may be prohibited. Some states require permits for air injection
- May require long-term monitoring and maintenance for bio-barrier type applications
- Effective remediation may only occur in more permeable layers or channels within an aquifer

4.4.9 Example Projects

In Situ Bioremediation at Port Hueneme - D, Oxnard, CA

A full-scale cleanup has been ongoing using *in situ* bioremediation to treat MtBE, BTEX, and TBA in groundwater at the Naval Base Ventura County, Port Hueneme in Oxnard, California. Geology at the site consists of a shallow sand aquifer bounded on the bottom by a clay aquitard, through which ground water flows at an average velocity of 1 ft/day. At a depth of 10-20 ft below ground surface (bgs), the 5,000- by 500-ft dissolved MtBE plume mixes with a smaller BTEX plume that originates from sands contaminated with residual nonaqueous phase liquid (NAPL).

The *in situ* bioremediation system consists of a 500-foot-wide "bio-barrier", which acts as a passive flow-through system and was installed just downgradient of the NAPL plume. Contaminated groundwater containing dissolved MtBE, TBA, and BTEX travels through the bio-barrier and is injected with various combinations of oxygen, air, and conditioned microorganisms. Oxygen gas and bioaugmented sections are located in the central core of the dissolved contaminant plume and air injections are used on the edge of the plume. Operation of the system began in the Fall of 2000. Initial MtBE, BTEX, and TBA concentrations in the groundwater plume were greater than 10,000 µg/L in the center of the plume.

After 18 months, contaminant concentrations were reduced to less than 5 µg/L in monitoring wells downgradient of the bio-barrier and extending across the length of the bio-barrier. No significant differences in performance were observed for the differently operated sections of the barrier. Dissolved oxygen increased from a pre-injection concentration below 1 mg/L to 10-35 mg/L throughout the treatment zone, thereby increasing the potential for aerobic biodegradation to occur. In addition, increased dissolved oxygen levels upgradient of the treatment zone due to dispersion of the injected gas appear to cause upgradient reductions in MtBE and benzene concentrations. Peripheral monitoring wells have not shown an increase in contaminant concentrations, indicating that groundwater is flowing through and not around the bio-barrier.

The biobarrier system includes 252 gas injection wells, 174 monitoring wells, 25 satellite gas storage tanks, 154 solenoid valves, a 240 ft3/hr-capacity oxygen generator, automated timer circuits, and associated piping and electrical lines. The total installation cost of this equipment was $435,000; initial year (FY 01) O&M costs were $75,000 and are expected to continue for a service life of 40 years. A preliminary cost comparison with an existing pump-and-treat system at this site suggests savings of more than $34 million over the project life. The state regulatory agency recently approved continued use of this biobarrier and installation of a second biobarrier (at the toe of the plume) as the final remedy for the MtBE plume (Miller 2002, ESTCP, 2003).

In Situ Bioremediation at Sunoco Service Station, MA

A full-scale cleanup was performed using in situ bioremediation to treat MtBE and BTEX at a service station in Massachusetts. Soil at the site consists of a layer of sand and gravel underlain by peat, silt, and clay. The *in situ* bioremediation system consisted of 12 injection wells and two butane injection panels used to stimulate cometabolic aerobic biodegradation of the contaminants in groundwater. The system was operated between October 2000 and January 2001. MtBE concentrations were reduced from 370 to 12 µg/L and BTEX contamination in groundwater was reduced by approximately two orders of magnitude during the 4 month period (Global BioSciences, Inc., 2001).

In Situ Bioremediation at South Beach Marina, Hilton Head, South Carolina

A full-scale cleanup was performed using in situ bioremediation to treat MtBE, BTEX, and naphthalene in groundwater at a service station with leaking underground fuel storage tanks. At this site, groundwater is 4.32 to 6.92 feet bgs, with an average hydraulic gradient of 0.078 feet/feet and with a calculated velocity of 6.42 feet per year. No confining units were identified at the site.

The in situ bioremediation application at this site included injection of a liquid microbial solution into the subsurface through monitoring and injection wells. This solution includes microbes (Pseudomonas, Bacillus, and Corynebacterium), oxygen, emulsifier, surfactant, and nutrients. Five injections were conducted. Over 3000 gallons was injected from February 1999 through September 2000 into approximately 40 wells and 15 Geoprobe® injection points. As of September 2000, MTBE levels decreased by 96% (from 3,310 to 146 µg/L), while benzene decreased by 83% (2,571 µg/L to 435 µg/L); toluene by 66% (24,330 µg/L to 8,300 µg/L), and naphthalene by 84% (5,377 µg/L to 853 µg/L); xylene levels increased and were above pre-operational level as of September 2000. The system will continue to be operated until all target levels have been met. The total cost for the cleanup of this site is $63,500; no additional information on cost breakdown was available (FRTR 2001).

4.5 *In Situ* Chemical Oxidation

Overview

- Injection of an oxidant and other amendments to convert site contaminants into innocuous products such as carbon dioxide and water
- EPA's MtBE Treatment Profiles Website dataset included use at 21 sites to treat MtBE
- Successful application depends on matching oxidant and delivery system to contaminants and site conditions

4.5.1 What is *In Situ* Chemical Oxidation?

In situ chemical oxidation (ISCO) is a technology in which an oxidant, and other amendments as necessary, is introduced into contaminated media to react with site contaminants such as MtBE, other fuel oxygenates, and other organic compounds, converting them to innocuous products, such as carbon dioxide and water. Typically, hydrogen peroxide (H_2O_2), ozone (O_3), or permanganate (MnO_4^-) oxidants have been used to treat MtBE in soil and groundwater. Persulfate ($S_2O_8^-$) compounds have also been used as chemical oxidants for treating MtBE. All of these chemicals react, either directly or through the generation of highly-reactive free radicals, such as OH•, and H•, or SO_4^-• with organic compounds such as MtBE to break hydrocarbon bonds and form degradation products such as alcohols, carbon dioxide, and water. In some applications, different oxidants may be used in combination, such as H_2O_2/O_3, or in conjunction with catalysts, such as H_2O_2 in the presence of ferrous iron (Fenton's chemistry or reagent), to enhance oxidation through the generation of free radicals. Depending on site conditions, oxidants may be introduced to the contaminated area using a variety of engineered approaches, including groundwater well injection, groundwater well recirculation, lance injection (jetting), PRBs, deep soil mixing, or soil fracturing (GWRTAC, 1999).

4.5.2 How Do the Properties of MtBE and Other Oxygenates Affect Treatment?

As with other organic and some inorganic contaminants, MtBE and other oxygenates are susceptible to degradation through oxidations reactions. If a sufficient amount and strength of oxidant and enough time are provided, all of the ether- and alcohol-based fuel oxygenates can be mineralized to carbon dioxide and water. For example, Figure 4.5-1 shows the equations for the stoichiometric mineralization of some of the common oxygenates through oxidation using hydrogen peroxide.

Figure 4.5-1. Stoichiometric Mineralization of Oxygenates Using Hydrogen Peroxide

ETBE, TAME, DIPE:	$C_6H_{14}O + 18\ H_2O_2$	$\rightarrow$	$6\ CO_2 + 25\ H_20$
MtBE:	$C_5H_{12}O + 15\ H_2O_2$	$\rightarrow$	$5\ CO_2 + 21\ H_20$
TBA:	$C_4H_{10}O + 12\ H_2O_2$	$\rightarrow$	$4\ CO_2 + 17\ H_20$
Ethanol:	$C_2H_6O + 6\ H_2O_2$	$\rightarrow$	$2\ CO_2 + 9\ H_20$
Methanol:	$CH_3O + 5/2\ H_2O_2$	$\rightarrow$	$CO_2 + 4\ H_20$

Analogous equations can be derived for mineralization using other oxidants. However, the oxidation of MtBE or other oxygenates to carbon and water is a multi-step, multi-path process in which each step has different equilibrium and kinetic factors that govern the extent and rate that each reaction can take place. Not all oxidants have proven successful in mineralization of MtBE, leaving by-products such as tert-butyl formate (TBF) and TBA. The full spectrum of possible reaction intermediates and governing criteria have not been determined for MtBE and the other oxygenates. However, in general, the greater number of carbon atoms in the oxygenate, the greater stoichiometric proportion of oxidant that will be required (under the same conditions) to fully oxidize it. For example, based on the equations in Figure 4.3-1, the complete mineralization of one pound of ETBE, MtBE, TBA, ethanol, and methanol would require 6.0, 5.7, 5.5, 4.4, and 2.7 pounds of hydrogen peroxide, respectively (Kelley, Marley, and Sperry, 2002).

While the above comparison (or similar comparisons for other oxidants) of the amount of oxidant required for different oxidants may hold under controlled laboratory conditions, the actual amount and type of oxidant that is necessary for the treatment of MtBE or other oxygenates at a given site will depend on numerous factors beyond the amount of contaminant present, including:

- The amount and types of other contaminants (such as other petroleum constituents) that will also consume oxidant

- The chemical composition of the soil and groundwater, specifically the amount of natural organic matter (NOM) and other reduced species, such as iron (II) or manganese (II); often analyzed as the chemical oxygen demand (COD) of the soil, or soil oxidant demand

- The pH, alkalinity, and temperature of the treatment area; these conditions will affect equilibrium and kinetic constants defining the extent and rate that each oxidation step can take place

- The potential for biodegradation of site contaminants or oxidation products

- Hydraulic and geologic parameters, such as hydraulic conductivity, hydraulic gradient, and permeability, that will affect the migration and dissolution of the oxidant once it is introduced to the subsurface

Because these factors can vary from site to site, typically field analyses of these parameters and bench- and pilot-scale studies are conducted to determine the type and amount of oxidant required for a specific application.

4.5.3 How is *In Situ* Chemical Oxidation Applied to Treat Oxygenates?

During ISCO, oxidants and any necessary amendments are introduced to the treatment area with one or more of the available delivery approaches. Pilot-scale testing is often used to determine the type of amendment and delivery system used at a given site. EPA policy regarding injection of supplements is discussed in Section 3.4. Some of the key considerations for the common oxidants and delivery approaches are summarized below.

Oxidants/Amendments

- **Hydrogen Peroxide (H_2O_2)** – Hydrogen peroxide has been used alone or in combination with other chemicals (such as using ferrous iron as a catalyst to generate free radicals through Fenton's chemistry) or with ultraviolet (UV) light. When used alone, hydrogen peroxide is typically injected as a concentrated solution (35-50%), which decomposes violently when contacting groundwater, generating heat and high volumes of gas. When using Fenton's chemistry, the pH of the treatment area is typically maintained at acidic ($pH < 4$) conditions and a more dilute hydrogen peroxide solution is used. Hydrogen peroxide and iron catalysts are typically injected separately, such as through specific ports in an injection lance, or through injection wells, because free radicals tend to react rapidly and can dissociate if generated prior to injection. Excess hydrogen peroxide that is not used in degrading organic compounds will rapidly degrade to water and oxygen (Leethem, 2001).

- **Ozone (O_3)** – Ozone is a highly reactive chemical that has been used to treat organic compounds in ex situ groundwater and drinking water treatment systems. It can also be used to treat MtBE in an ozone-air sparging system. This system injects ozone through tubing to a microporous sparge point designed to generate very small bubbles ("microbubbles", approximately 50 micrometers (μm) in diameter), which have a high surface-to-volume ratio. Organic contaminants in groundwater, such as MtBE, volatilize into the ozone bubbles and are oxidized. Ozone that is not consumed degrades to oxygen. Ozone is often used in combination with other oxidants, such as hydrogen peroxide, to enhance oxidation through the generation of free radicals. If bromine is present in the treatment area, bromate generation, which can occur during ozonation, is typically monitored during treatment.
- **Permanganate (MnO_4^-)** – Permanganate is often employed in the form of solid or a solution of potassium or sodium permanganate for groundwater treatment. It has a smaller oxidizing potential than ozone and hydrogen peroxide using Fenton's chemistry, resulting in the relatively slower oxidation of MtBE and other oxygenates. However, permanganate has a longer half-life compared to the stronger oxidants, and persists in the environment for a longer time. The end product of permanganate oxidation is manganese dioxide, which, depending on the groundwater pH, can precipitate into the formation. Excessive precipitation may reduce soil permeability.
- **Other Oxidants** – Combinations of the above oxidants and other oxidants such as persulfate compounds are also being used to treat MtBE and other oxygenates. These and other combinations and other oxidants are being developed to maximize the generation of highly-oxidizing free radicals, increase oxidant persistence, or otherwise enhance *in situ* oxidation.

Delivery Approaches

- **Groundwater Well Injection** – Oxidants may be introduced to the treatment zone through existing or new groundwater monitoring wells either as a liquid, gas, or solid. This method relies on the natural migration of oxidants from the well into the formation. Injection wells need to be adequately spaced to allow for oxidant delivery to the entire treatment area.
- **Groundwater Recirculation** – A groundwater recirculation system may be used to extract groundwater from within or at the downgradient edge of the contaminated area, introduce oxidants and amendments aboveground, and reinject the groundwater upgradient of the treatment area. This approach can be used to increase the flow-through of oxidant through the treatment area, as well as to achieve downgradient containment of a contaminated groundwater plume.
- **Lance Injection, Jetting, Fracturing** – Use of a high-pressure lance can create micro-fractures in soils that increase soil permeability and allow for direct injection of oxidants and amendments into a desired treatment area without the need for an existing or new groundwater well.
- **Soil Mixing** – For lower permeability soils, soil mixing using tilling for shallow soil or an auger for deeper soil can be used to introduce oxidants to a treatment area.
- **PRB** – Oxidants can be injected into the treatment zone of a PRB to oxidize the groundwater that flows through it. This approach can be used as a containment approach for a contaminated groundwater plume. Also, a PRB could be placed upgradient or within a treatment area allowing the oxidized groundwater leaving the PRB to flow through the treatment area.

There are also technologies that use electrical or other forms of energy to generate oxidizing and reducing radicals in aqueous solution and thereby destroy contaminants such as MtBE and other oxygenates. These technologies include ultrasound and electron beam treatment, and are primarily used in *ex-situ* applications (see Section 4.6). Recently, however, ultrasound treatment has been proposed as a potential *in-situ* application by incorporating ultrasonic transducers into a robotic self-powered mining head (Chang and Yen 2000).

Additional information relevant to the application of ISCO at sites in general or contaminated with MtBE and other oxygenates is available in the following documents:

- Kelley, Marley, and Sperry, 2003. In Moyer and Kostecki, Eds. 2003. *MtBE Remediation Handbook.* Amherst Scientific Publishers.
- Ground-Water Remediation Technologies Analysis Center. 1999. *Technology Evaluation Report, In Situ Chemical Treatment (TE-99-01)*. Prepared by Yin, Y. and Allen, H.E. July. http://www.gwrtac.org/pdf/inchem.pdf
- Interstate Technology and Regulatory Cooperation Work Group. 2001. Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater. June. http://www.itrcweb.org/ISCO-1.pdf
- Naval Facilities Engineering Service Center. Chemical Oxidation, In-Situ Technology Web Page. http://enviro.nfesc.navy.mil/erb/restoration/technologies/remed/phys_chem/phc-43.asp
- Strategic Environmental Research and Development Program (SERDP). 2003. In Situ Chemical Oxidation Initiative. http://www.serdp-estcp.org/ISCO.cfm

4.5.4 What Types of Projects Involve *In Situ* Chemical Oxidation for Oxygenates?

From the 323 MtBE projects in EPA's MtBE Treatment Profiles dataset, 21 projects were identified where MtBE was treated using *in situ* chemical oxidation. No ISCO projects reported treating other oxygenates. Four of the projects used ozone and 17 used hydrogen peroxide either alone or with Fenton's chemistry.

Table 4.5-1 summarizes the scale and operational status for the 21 ISCO projects. The data used to compile this information was current at the time the profile for each project was completed. Short summaries for two projects, *Ozone Sparging at Former Service Station, Bucks County, PA* and *Fenton's Chemistry at a Warehousing Facility, Union, NJ*, are included at the end of this section, with additional information about all 21 projects provided in Appendix A.

Table 4.5-1. General Information on 21 *In Situ* Chemical Oxidation Projects

Technology(ies)	# of Projects	Operational Status		Scale		
		Completed	Ongoing	Bench	Pilot	Full
In situ Chemical Oxidation Only	14	6	8	0	4	10
In situ Chemical Oxidation with Air Sparging	2	0	2	0	0	2
In situ Chemical Oxidation with Pump-and-Treat	1	1	0	0	0	1
In situ Chemical Oxidation with SVE	2	1	1	0	0	2
In situ Chemical Oxidation with Multiple Phase Extraction	2	0	2	0	0	2
TOTAL	**21**	**8**	**13**	**0**	**4**	**17**

As shown in Table 4.5-1, most of the 21 ISCO projects were performed at full scale (17 projects) at the time that their profiles were compiled. Eight of the 21 projects were identified as completed, and the remaining 13 as ongoing. In addition, while most (14) of the projects used ISCO alone, 7 projects supplemented ISCO with air sparging, pump-and-treat, SVE, or MPE.

4.5.5 How Has *In Situ* Chemical Oxidation Performed in Treating Oxygenates?

Tables 4.5-2 and 4.5-3 summarize performance data for the 8 completed and 13 ongoing ISCO projects. The data presented in these tables show that ISCO (either alone or in combination with other technologies) has been used to remediate MtBE in groundwater from concentrations greater than 10,000 µg/L to less than 50 µg/L and has achieved MtBE concentration reductions greater than 99 percent. Because the dataset included relatively few completed projects with performance data, Table 4.5-2 provides a summary of specific projects instead of a summary of minimum, median, and maximum concentrations. The median project duration for the 19 completed sites ranged from 9 to 18 months. None of the projects reported performance data for other oxygenates.

Table 4.5-2. Completed *In Situ* Chemical Oxidation Projects - Performance Summary for 8 Projects

Technology(ies)	**Site Name and Location**	**Scale**	**Initial MtBE Concentration [1] (µg/L)**	**Final MtBE Concentration [1] (µg/L)**	**Median Project Duration (months)**
In situ Chemical Oxidation Only	Former Maintenance and Repair Garage, NY – H, West Chester, NY	Pilot	451	171	12
In situ Chemical Oxidation Only	Spill Site (Long Island, New York), Long Island, NY	Pilot	6,300	79	2
In situ Chemical Oxidation Only	Service Station, PA – D, Warminster, PA	Full	50,000	6.6	14
In situ Chemical Oxidation Only	Service Station, NJ – E, North Halden, NJ	Full	403,000	1,430	2
In situ Chemical Oxidation Only	Garage, NJ – F, Island Heights, NJ	Full	55	4	14
In situ Chemical Oxidation Only	Warehousing Facility in Union County New Jersey, NJ	Full	6,400	70	NR
In situ Chemical Oxidation with SVE	Former Service Station, PA – A, Bucks County, PA	Full	475,000	68,400	18
In situ Chemical Oxidation with Pump-and-Treat	North Texas Service Station, TX	Full	17,000	31	9

Notes:

NR Information not provided

[1] Treatment performance data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website, as shown in cluin.org/products/mtbe, and summarized in Appendix A. Appendix A shows the specific sites that are summarized here, along with technology design, operation, and performance data for each of the projects.

[2] Performance data are shown in terms of changes in concentration of MtBE in the groundwater, as provided in the reference materials and from the project contacts, except as noted. MtBE concentrations prior to beginning treatment (shown as "initial concentration") and after treatment was completed (shown as "final concentration") are provided. For projects where more than one technology was used, performance data are presented under each of the technologies used for the project.

Table 4.5-3. Ongoing *In Situ* Chemical Oxidation Projects - Performance Summary for 13 Sites

MtBE Concentration Range	# of Projects Reporting Initial MtBE Concentrations	# of Projects with Last Reported MtBE Concentrations
Greater than 100,000 µg/L	0	0
Greater than or equal to 10,000 µg/L but less than 100,000 µg/L	1	0
Greater than or equal to 1,000 µg/L but less than 10,000 µg/L	3	2
Greater than or equal to 100 µg/L but less than 1,000 µg/L	6	2
Greater than or equal to 50 µg/L but less than 100 µg/L	0	1
Less than 50 µg/L	2	6

4.5.6 What Are the Costs of Using *In Situ* Chemical Oxidation to Treat MtBE?

The total project cost was reported for 1 of the 21 ISCO projects identified above. The completed Former Service Station, PA – A project, which employed used ISCO with SVE, reported a total project cost of $146,000. This cost was broken down further into $90,000 of capital cost and $56,000 of operation and maintenance cost. Because the area, volume, or mass treated was not available for this project, no unit cost was calculated.

There is little additional information in the literature about the costs of using ISCO for the treatment of MtBE and other oxygenates, or for other contaminants. The cost per volume of subsurface treated (identified as cubic yards of subsurface) was reported in one literature source as ranging from $52 to $310 per cubic yard in general (GWRTAC, 1999). The cost of ISCO generally is considered to be average, among the costs for remediation technologies, for treatment of contaminated groundwater (FRTR, 2002).

4.5.7 What Factors May Affect the Performance and Cost of Oxygenate Treatment using *In Situ* Chemical Oxidation?

When MtBE or other oxygenates are present and must be remediated at a site, ISCO, either alone or in combination with other technologies, may be a suitable remediation approach. Although both ether- and alcohol-based oxygenates are susceptible to chemical oxidation, the chemical, hydraulic, and geologic conditions of a given site will determine whether ISCO is a feasible option for treatment. For example, ISCO may not be economically feasible for sites with high concentrations of NOM or other constituents that may consume large amounts of oxidant. In addition, sites with low subsurface permeability may require more complex approaches, such as fracturing or soil mixing, to deliver the necessary oxidant to the treatment zone, potentially increasing costs. Other site characteristics, such as pH, alkalinity, and temperature will also affect system design and impact cost and performance. For example, for oxidants that have specific pH requirements, pretreatment of the aquifer with an acid solution to lower the pH is typically considered. In addition, off-gas generated by the chemical reactions in ISCO may require capture and treatment (Kelley, Marley, and Sperry, 2002).

In addition to the technology-specific factors described above, additional factors may also affect the performance and cost of an ISCO system. These factors include: the concentration, mass, and distribution of contaminants in the groundwater; subsurface geology and hydrogeology; cleanup goals; and requirements for site cleanup. For example, heterogeneity within the subsurface may result in preferential pathways that prevent injected oxidant from reaching the entire treatment area.

Because of the above factors, the design of an ISCO system is typically based on pilot-scale testing rather than generic design equations. More information about the factors that influence the performance and cost of ISCO systems in general is available in the references listed in this report.

4.5.8 Conclusions

Data from In Situ Chemical Oxidation MtBE Treatment Profiles

- Used to remediate groundwater contaminated with MtBE, but less frequently than some other technologies, such as air sparging and bioremediation – it was employed at 21 of the 323 (6.5%) of the projects in the dataset
- Most often used alone (67% of projects in dataset); to a lesser extent has been employed in conjunction with pump-and-treat or other technologies
- The cost common oxidant applied was hydrogen peroxide with ferrous iron (Fenton's chemistry)
- Used to remediate MtBE in groundwater from concentrations greater than 10,000 µg/L to less than 50 µg/L and has achieved MtBE concentration reductions greater than 99 percent
- Median project duration is approximately 1 year
- Cost information is limited – one project reported total project cost of $146,000

Treatability of MtBE and Other Oxygenates Using In Situ Chemical Oxidation

- All ether- and alcohol-based oxygenates susceptible to chemical oxidation
- In general, the greater number of carbon atoms in the oxygenate, the greater stoichiometric proportion of oxidant will be required (under the same conditions) to fully oxidize
- Applicability to given site based primarily on factors not related to type of oxygenate (that is, all oxygenates can be treated using chemical oxidation, but certain other site conditions, like high concentrations of native organic matter or low permeability, may make other treatment technologies more attractive)

Other Potential Advantages of Applying In Situ Chemical Oxidation (EPA, 1995; FRTR, 2002)

- Has potential to be used to target hot spots that may not be amenable to bioremediation
- Has potential to achieve cleanup goals in relatively short amount of time (several months to a year)
- Depth of application is only limited to the delivery approach used

Other Potential Limitations to Applying In Situ Chemical Oxidation (EPA, 1995; FRTR, 2002)

- Relatively large amount of oxidant may be needed for treatment of large masses of contaminant (oxidant does not target only the contaminants of concern)
- May have low contact between oxidant and contaminant in heterogeneous media or in areas with low permeability
- Special precautions may need to be taken to protect worker health and safety during operation (because of use of strongly oxidizing chemicals); also concentrated oxidant injection can result in violent subsurface reactions
- Chemical reactions may form toxic by-products (such as bromate during ozone oxidation) in the groundwater
- Off-gas may require capture and treatment

4.5.9 Example Projects

Ozone Sparging at Former Service Station, Bucks County, PA

At a former service station located in Bucks County, PA, remediation needed to be completed within nine months to facilitate the sale of the property. The cleanup approach used ozone sparging, pump-and-treat, MPE, and SVE to treat MtBE. Free product was removed prior to performing ozone sparging. The sparging system consisted of multiple, nested sparge wells in a treatment area of 180 ft by 150 ft, and used an ozone dosage of 2.5 lbs/day at 2 scfm over a 4 month period. MtBE concentrations in groundwater were reduced from 17,000 µg/L to 31 µg/L, which was below the cleanup level of 2,900 µg/L. The total cost reported for treatment was $146,000, consisting of $90,000 for capital and $56,000 for O&M (EPA, 2002a).

Fenton's Chemistry at Warehousing Facility in Union County New Jersey, Union City, NJ

Groundwater at an operating warehousing facility in Union, NJ was contaminated with MtBE (concentrations up to 6,400 µg/L), TBA, and BTEX. Soil at the site consists of soft red shales interbedded with harder sandstones and minor amounts of conglomerate. After completing a pilot study, hydrogen peroxide and catalysts were injected at six points during three treatment cycles over a three-month period in mid-1996 (each cycle consisted of 15 days injection followed by 15 days without injection). MtBE concentrations in groundwater were reduced to less than 5 µg/L, which was below the cleanup level of 70 µg/L. Rebound was evaluated four months after treatment was complete; results remained below the cleanup level. There was no current cost data provided for this site (EPA, 2002a).

4.6 Groundwater Pump-and-Treat and Drinking Water Treatment

Overview

- Extraction of contaminated groundwater from the subsurface and treatment using one or more *ex situ* technologies
- EPA's MtBE Treatment Profiles Website dataset includes use during 100 projects to treat MtBE or other oxygenates
  - 85 pump-and-treat projects
  - 15 drinking water treatment projects
- Used to reduce the concentration and mass of MtBE or other oxygenates from groundwater or for hydraulic containment

4.6.1 What is Groundwater Extraction for Pump-and-Treat and Drinking Water Treatment?

Groundwater pump-and-treat involves the extraction of groundwater from a contaminant plume and the treatment of extracted water using one or more aboveground technologies. Drinking water treatment systems where the extracted water is contaminated with fuel oxygenates involves many of the same activities as groundwater pump-and-treat. In general, the methods for extraction of the groundwater are not linked to or limited by the aboveground (*ex situ*) treatment technologies. This section focuses on groundwater extraction, while the following section (Section 4.7) focuses on above-ground treatment of extracted groundwater, for both pump-and-treat and for drinking water treatment.

The groundwater extraction component typically consists of multiple wells and/or trenches for extraction of groundwater and includes differential control of extraction rates from individual wells to optimize operation. Most groundwater extraction systems incorporate extraction wells that are installed within the contaminant plume downgradient from the source. These extraction wells are designed and controlled to act as a barrier to additional downgradient movement of the contaminant plume and, over a long period of time, to extract contaminant mass. Due to the water solubility of MtBE and other oxygenates, and the associated occurrence of significant quantities of contaminant mass in the dissolved phase, such groundwater extraction systems have specific application to the remediation of plumes incorporating oxygenate contamination.

4.6.2 How Do the Properties of MtBE and Other Oxygenates Affect Groundwater Extraction?

The properties of MtBE and other oxygenates are relevant to both the extraction and treatment components of pump-and-treat. As discussed in Section 2.6, the properties of fuel oxygenates, specifically their relatively high aqueous solubility and low tendency to partition to organic matter, affect how they migrate with groundwater. As a result, oxygenates tend to become dissolved in and migrate with groundwater more readily than other petroleum contaminants such as BTEX. One consequence of this tendency that is beneficial to pump-and-treat remediation is that oxygenates are also more readily extracted with groundwater than other contaminants.

4.6.3 How is Pump-and-Treat Applied to Treat Oxygenates?

A pump-and-treat system consists of an extraction and a treatment component. Groundwater is typically extracted through vertical groundwater recovery wells although, in the last decade or so, horizontal wells and trenches have also been employed. Variables in the design of a typical system include (EPA, 2001d):

- Types of extraction systems to be used
- Number and location of extraction points
- Design of extraction points (for example, diameter, depth and well screen interval)
- Type of pumping apparatus to employ (for example, aboveground vacuum, submersible, pneumatic)
- Design of a distribution system to transport extracted groundwater to the aboveground treatment system (for example, aboveground vs. underground piping or possible need for double-walled piping at RCRA-regulated sites)

For the most part, the above considerations are not affected by the specific contaminants present at the site, but by site characteristics, such as plume distribution, hydrogeologic characteristics, and above-ground obstacles (such as buildings or active roadways). Typical extraction system construction materials, such as polyvinyl chloride (PVC) piping and stainless steel pumps, are appropriate for fuel oxygenates at typical contaminated groundwater concentrations. Groundwater extraction system optimization approaches at sites contaminated with MtBE and other oxygenates are similar to those used at other sites, such as use of phased construction, adaptive management of pumping rates, periodic modeling of the well arrays, and pulsed pumping (Li *et al*, 2003).

A conventional pump-and-treat extraction system is typically designed to recover only groundwater. Integrated or separate systems have also been used to capture free product or contaminated vapor concurrently with groundwater. Extraction systems that incorporate the integrated recovery of multiple phases are discussed in Section 4.3 (MPE) and separate systems to recover these other phases are discussed in Section 4.2 about SVE and Section 5.2 about free product recovery.

More detailed information relevant to the application of pump-and-treat at sites contaminated with MtBE and other oxygenates and in general is available in the following documents:

- Cohen, R.M., J.W. Mercer, and R.M. Greenwald. 1998. *EPA Groundwater Issue, Design Guidelines for Conventional Pump-and-Treat Systems.* EPA 540/S-97/504. September. http://www.epa.gov/ada/issue.html.

- Li, Tie, U. Raaj, P.G. Patel, D.K. Ramsden, and J. Greene. 2003. "Groundwater Recovery and Treatment". In Moyer and Kostecki, Eds. *MtBE Remediation Handbook.* Amherst Scientific Publishers.

- California MtBE Research Partnership. 2000. *Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MtBE) from Drinking Water, Second Edition.* February.

4.6.4 What Projects Have Involved Pump-and-Treat for Treating Oxygenates?

From the 323 projects in EPA's MtBE Treatment Profiles dataset, 85 projects were identified where MtBE in groundwater was remediated using pump-and-treat along with 15 additional projects that treated MtBE in drinking water (collectively referred to as pump-and-treat projects). Information on the treatment of other oxygenates was reported for 20 of these 100 projects: 16 projects reported TBA, 6 projects reported TAME, 2 projects reported ethanol, and 1 project reported DIPE as a contaminant in addition to MtBE.

Table 4.6-1 summarizes the scale and operational status for the 100 pump-and-treat projects. Short summaries for two complete pump-and-treat projects, *Pump-and-treat at Christy Station, North Windham, ME* and *Pump-and-treat and SVE at Service Station NH-B, NH*, are included at the end of this section.

Table 4.6-1. General Information about 100 Pump-and-Treat Projects

Technology(ies)	# of Projects	Operational Status		Scale		
		Completed	Ongoing	Bench	Pilot	Full
Pump-and-Treat Only	45	12	33	0	13	32
Pump-and-Treat with Air Sparging and SVE	18	5	13	0	0	18
Pump-and-Treat with SVE	14	1	13	0	1	13
Pump-and-Treat with Air Sparging	4	2	2	0	0	4
Pump-and-Treat with Other Technologies	4	1	3	0	1	3
Drinking Water Treatment	15	1	14	0	1	14
TOTAL	**100**	**22**	**78**	**0**	**16**	**84**

Note: Fifteen (15) drinking water treatment projects are included

As shown in Table 4.6-1, most of the 100 pump-and-treat projects were full scale (84 projects) and were ongoing (78 projects) at the time that its profile was published. In addition, while most (54%) of the projects used pump-and-treat alone, almost half supplemented pump-and-treat with air sparging, SVE or other technologies, such as phytoremediation, bioremediation, or ISCO.

4.6.5 How Has Pump-and-Treat Performed in Treating Oxygenates?

For the 100 pump-and-treat projects in the dataset, initial concentrations in groundwater were as high as 475,000 µg/L (North Texas Service Station, TX). Concentrations after treatment were as low as non-detectable (the typical reporting limit for MtBE is 5 µg/L). Tables 4.6-2 through 4.6-5 summarize available MtBE and TBA performance data for pump-and-treat projects.

The data presented in Table 4.6-2 for 21 completed pump-and-treat projects (either alone or in combination with other technologies) shows that MtBE concentration reductions in groundwater of greater than 99 percent have been achieved in several projects. The median project duration for the 21 completed sites ranged from 1.5 to 5.5 years.

Table 4.6-2. MtBE Performance Summary for 21 Completed Pump-and-Treat Projects

Technology(ies)	# of Projects	Initial MtBE Concentration [1] (µg/L)			Final MtBE Concentration [1] (µg/L)			Median Project Duration (months)
		Minimum	Median	Maximum	Minimum	Median	Maximum	
Pump-and-Treat Only (groundwater)	8	96	1,800	8,000	2	24	68	27
Pump-and-Treat with Air Sparging and SVE	5	3	10	390	2	3	4.8	50
Pump-and-Treat with Other Technologies	4	1,200	11,000	475,000	18	2,070	68,400	40

Notes:

[1] Treatment performance data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website, as shown in cluin.org/products/mtbe, and summarized in Appendix A. Appendix A shows the specific sites that are summarized here, along with technology design, operation, and performance data for each of the projects.

[2] Performance data are shown in terms of changes in concentration of MtBE in the groundwater, as provided in the reference materials and from the project contacts, except as noted. MtBE concentrations prior to beginning treatment (shown as "initial concentration") and after treatment was completed (shown as "final concentration") are provided. For projects where more than one technology was used, performance data are presented under each of the technologies used for the project.

Treatment performance data for ongoing projects are shown on Tables 4.6-3 and 4.6-4, for pump-and-treat and drinking water treatment projects, respectively. Both types of projects treated groundwater with relatively high initial MtBE concentrations (greater than 100,000 µg/L). The available data show that 10 of 11 drinking water treatment projects achieved treated MtBE concentrations of less than 50 µg/L, while the results for pump-and-treat were more widely distributed.

Table 4.6-3. MtBE Performance Summary for 62 Ongoing Pump-and-Treat Projects

MtBE Concentration Range	# of Projects Reporting Initial MtBE Concentrations	# of Projects with Last Reported MtBE Concentrations
Greater than 100,000 µg/L	4	1
Greater than or equal to 10,000 µg/L but less than 100,000 µg/L	11	2
Greater than or equal to 1,000 µg/L but less than 10,000 µg/L	14	5
Greater than or equal to 100 µg/L but less than 1,000 µg/L	11	3
Greater than or equal to 50 µg/L but less than 100 µg/L	3	2
Less than 50 µg/L	10	13

Table 4.6-4. MtBE Performance Summary for 12 Ongoing Drinking Water Treatment Systems

MtBE Concentration Range	# of Projects Reporting Initial MtBE Concentrations	# of Projects with Last Reported MtBE Concentrations
Greater than 100,000 µg/L	3	0
Greater than or equal to 10,000 µg/L but less than 100,000 µg/L	2	0
Greater than or equal to 1,000 µg/L but less than 10,000 µg/L	5	0
Greater than or equal to 100 µg/L but less than 1,000 µg/L	1	1
Greater than or equal to 50 µg/L but less than 100 µg/L	0	0
Less than 50 µg/L	1	10

Table 4.6-5 provides a summary of treatment performance data for 9 pump-and-treat projects that provided performance data for TBA. Initial TBA concentrations were as high as 17,000 µg/L, with most after-treatment concentrations less than 50 µg/L. Due to the additional interest in TBA, a review of data for the 390 projects in the database as of April 2004 showed a total of 15 pump-and-treat projects reporting performance data for TBA. Most of these projects reported using the HiPOx process for treatment of extracted groundwater, with additional projects using GAC treatment.

Table 4.6-5. TBA Performance Data for 9 Pump-and-Treat Projects

Concentration Range	# of Projects Reporting Initial Concentrations	# of Projects with Last Reported Concentrations
Greater than 100,000 µg/L	0	0
Greater than or equal to 10,000 µg/L but less than 100,000 µg/L	1	0
Greater than or equal to 1,000 µg/L but less than 10,000 µg/L	4	1
Greater than or equal to 100 µg/L but less than 1,000 µg/L	4	0
Greater than or equal to 50 µg/L but less than 100 µg/L	0	0
Less than 50 µg/L	1	7

4.6.6 What Costs Have Been Associated with Using Pump-and-Treat in Treating MtBE?

Project cost data were reported for 43 of the 100 pump-and-treat projects in the dataset; these include data for both ongoing and completed projects. In most cases, the components that make up the project costs were not reported. However, it is likely that these costs incorporate different components, such as treatment, monitoring, design, oversight, and health & safety. Most (40 projects) of the reported costs were for ongoing projects and represent either a partial actual cost as of the time that the report was made or an estimated total project cost.

Tables 4.6-6 summarize the cost information from these 43 projects, broken down by type of other technologies used in conjunction with pump-and-treat.

Table 4.6-6. Cost Summary for 43 Pump-and-Treat and Drinking Water Treatment Projects

Technology(ies)	# of Projects	Total Cost Range ($)		Median Total Reported Cost ($)
		Minimum	Maximum	
Pump-and-Treat Only	15	71,900	1,120,000	500,000
Pump-and-Treat with Air Sparging and SVE	9	96,400	567,000	327,000
Pump-and-Treat with Air Sparging	1	672,000	672,000	672,000
Pump-and-Treat with SVE	7	160,000	624,000	339,000
Pump-and-Treat with Other Technologies	1	65,000	65,000	65,000
Drinking Water Treatment	10	119,000	4,000,000	245,000

Another source reported the unit costs of pump-and-treat (based only on capital cost) as less than $20 per 1,000 gallons per year for projects treating more than 20 million gallons of groundwater per year, and unit costs (based on O&M cost) as less than $5 per 1,000 gallons per year for projects treating more than 20 million gallons of groundwater per year (EPA, 2001d). These unit costs represent treatment costs for use of pump-and-treat in general, and are not specific to the treatment of MtBE and other oxygenates. In another source, the cost of pump-and-treat generally is considered to be worse than average, among the costs for remediation technologies, for treatment of contaminated groundwater (FRTR, 2002).

4.6.7 What Factors May Affect the Performance and Cost of Oxygenate Treatment Using Pump-and-Treat?

Because of the high water solubility of oxygenates, groundwater extraction may be effective in removing a significant mass of these contaminants. Key factors that affect the performance and cost of the extraction component of a pump-and-treat system include:

- The depth and accessibility of the plume; site hydrogeologic characteristics, such as aquifer permeability
- The hydraulic conductivity, and flow gradient
- Remedial goals for the site
- The presence or prior removal of the contaminant source

If groundwater contamination is deep or beneath areas (such as buildings and rail lines) where conventional vertical wells cannot be placed, innovative drilling techniques or more powerful extraction pumps may be required. Alternatively, shallow and accessible groundwater may be easily extracted using simple collection trenches. Hydrogeologic characteristics will define the number, design, and spacing of extraction points, with tighter formations typically requiring more extraction points for a given area. Groundwater flow characteristics and the number and spacing of wells will be the basis for determining the flow rate of groundwater that needs to be extracted to achieve the desired capture zone. Cleanup goals are also a factor. On-site containment goals may require only pumping from the downgradient edge of a plume, whereas a goal of complete aquifer restoration may require more well points pumping at a higher extraction rates.

One of the most significant factors that affect cost and performance is whether the contaminant source area at a site is present. If a contaminant source area is allowed to continue to contribute to the groundwater plume, groundwater extraction may be required for much longer periods of time than if the contaminant source is removed or treated prior to beginning groundwater pump-and-treat. Because they are relatively water soluble, oxygenates tend to dissolve in groundwater rather than form NAPL. When they do form NAPL, they float rather than sink, and thus form an LNAPL. Thus, removal or treatment of MtBE and other oxygenate source areas can be more straightforward than for other contaminants such as chlorinated solvents.

4.6.8 Conclusions

Based on the information available from the pump-and-treat projects listed in the MtBE Treatment Profiles Website dataset and other information contained in the reference documents reviewed in preparation of this report, the following conclusions were identified regarding the use of pump-and-treat to remediate sites contaminated with MtBE and other oxygenates.

Data from Pump-and-Treat MtBE Treatment Profiles

- Has commonly been used to remediate groundwater contaminated with MtBE and other oxygenates – it was employed at 85 of the 323 (26%) of the projects in the dataset (drinking water treatment projects represented an additional 15 projects in the dataset)
- Most often used alone or in conjunction with air sparging and SVE; to a lesser extent, has been employed in conjunction with other technologies
- Has achieved MtBE concentration reductions greater than 99 percent in several projects
- Median project duration ranged from 1.5 to 5.5 years
- Median reported total cost was approximately $500,000 for pump-and-treat alone

Treatability of MtBE and Other Oxygenates Using Pump-and-Treat

- Groundwater Extraction – Fuel oxygenates are relatively well suited to removal with extracted groundwater

Other Potential Advantages of Applying Pump-and-Treat (EPA, 1995; FRTR, 2002)

- Properties of MtBE (high water solubility and low organic/water partition coefficient) make it amenable to groundwater extraction
- Can be used to remediate an aquifer or to provide for hydraulic containment

Other Potential Limitations to Applying Pump-and-Treat (EPA, 1995; FRTR, 2002)

- Long-term operation may be required to achieve remediation goals for large plumes, complex hydrogeologies, or if an active source remains in place
- The cost of constructing, operating, and maintaining treatment systems is considered to be relatively high
- Biofouling or mineral precipitation in extraction wells or treatment processes can reduce system performance

4.6.9 Example Projects

The following two project descriptions incorporate examples of completed, full-scale applications of pump-and-treat technology to MtBE-contaminated sites:

Pump-and-Treat at Christy Station, North Windham, ME

MtBE was detected in groundwater at Christy Station, located in North Windham, Maine, soon after the fuel station was constructed in 1997. Between May and June 1998, a full-scale cleanup was performed using a pump-and-treat system that consisted of two extraction wells operating at a combined 3 gpm. Extracted groundwater was treated using shallow tray aeration followed by GAC, and the treated groundwater was disposed off site. Initial concentrations of MtBE in groundwater were as high as 6,000 µg/L, but MtBE concentrations stabilized at 300 µg/L with the operation of the pump-and-treat system. The goal was to reduce MtBE in the aquifer to concentrations less than 500 µg/L. Following aeration, MtBE in extracted groundwater was reduced to concentrations ranging from 10 to 30 µg/L and following GAC adsorption, MtBE was reduced to concentrations of less than 2 µg/L. A performance standard for extracted groundwater was not identified. The cost assessment for the remediation was $200,000, the capital cost for the pump-and-treat system was $60,000 and the O&M cost was $11,000 for 1 month of operation (Eremita, 2000).

Pump-and-Treat and SVE at Service Station NH-B, Somersworth, NH

During inventory measurements in September 1996, a gasoline station in New Hampshire, referred to as Service Station NH-B, detected a release of 2,100 gallons of gasoline. Soil at the site consists of 4 to 8 ft of sandy fill overlying 2 to 13 ft of glacial till, with bedrock occurring at 10 to 15 ft below ground surface (bgs). The depth to groundwater ranges from is 5 to 15 ft bgs. The site is characterized by fractured bedrock and a hydraulic gradient of 30 ft/1,000 ft. Remedial activities included the removal of 3 USTs, 860 tons of contaminated soil, 27,000 gals of groundwater containing 158 lbs of hydrocarbons, and 120 gals of light non-aqueous phase liquids (LNAPL). A pump-and-treat system consisting of 7 recovery wells screened to bedrock and operating at a total flow rate of 7.5 gpm was implemented. Extracted groundwater was treated using oil/water separation, filtration, and air stripping. The air stripper contained a 7 horse power (HP) blower which operated at 1,000 scfm. Maximum concentrations in the influent to the air stripper were 1,670,000 µg/L of MtBE and 439,000 µg/L of BTEX. SVE was conducted using 11 vertical wells and 4 horizontal wells, and a 15 HP blower operated at 300 scfm and 3.5 to 5 inches of mercury. No vapor treatment was performed. As of January 2000, pump-and-treat system had removed 4,300 lbs of hydrocarbons and SVE had removed 2,976 lbs of hydrocarbons. They currently use performing enhanced bioremediation at the site. The current total remediation cost for this site is $590,000 (EPA, 2002a).

4.7 Treatment of Extracted Groundwater Used in Pump-and-Treat and Drinking Water Treatment Systems

- EPA's MtBE Treatment Profiles Website dataset includes use at 70 projects to treat MtBE or other fuel oxygenates
- Common processes such as air stripping and adsorption may not be as effective for oxygenates as for common fuel components such as BTEX

4.7.1 What is Above-Ground Treatment for Extracted Groundwater?

The above-ground (*ex situ*) treatment technologies used for extracted groundwater are applied both in pump-and-treat systems and drinking water treatment systems. In general, the methods for extraction of groundwater are not linked to or limited by the type of above-ground treatment technologies. This section focuses on above-ground treatment of extracted groundwater, for both pump-and-treat and drinking water treatment, while the previous section (Section 4.6) focuses on groundwater extraction. This section also includes specific examples of treatment applications used in pump-and-treat and drinking water treatment systems.

The general types of aboveground technologies that have been used for treating extracted groundwater that is contaminated with MtBE and other oxygenates include the following (California MtBE Research Partnership, 2000):

- **Air Stripping** – Processes in which contaminants are volatilized from water to air in an engineered system, such as a packed tower; treatment of the resulting contaminated vapor phase may also be required
- **Adsorption** – Processes in which contaminants are adsorbed from water onto a medium, such as granular activated carbon (GAC) or resin, as driven by equilibrium forces
- **Chemical Oxidation** – Processes in which contaminants are sequentially oxidized to less toxic products through the introduction of chemical oxidants or the creation of oxidizing conditions through other means, such as using ultraviolet (UV) radiation, electrical stimulation, or cavitation
- **Biotreatment** – Processes in which contaminants are biodegraded in an engineered system, such as an attached growth or activated-sludge bioreactor

4.7.2 How Do the Properties of MtBE and Other Oxygenates Affect Treatment?

The properties of MtBE and other oxygenates affect their relative treatability in extracted water using different technologies. Air stripping, adsorption, oxidation, and biotreatment technologies are technically capable of and have been used to treat water contaminated with some or all of the fuel oxygenates. However, the properties of oxygenates versus other fuel contaminants such as BTEX, and the different properties of ether-based versus alcohol-based oxygenates, are important to consider when selecting and designing an above-ground treatment system. The effect of fuel oxygenate' properties on treatment using each of the commonly used technologies is briefly discussed below.

Air Stripping

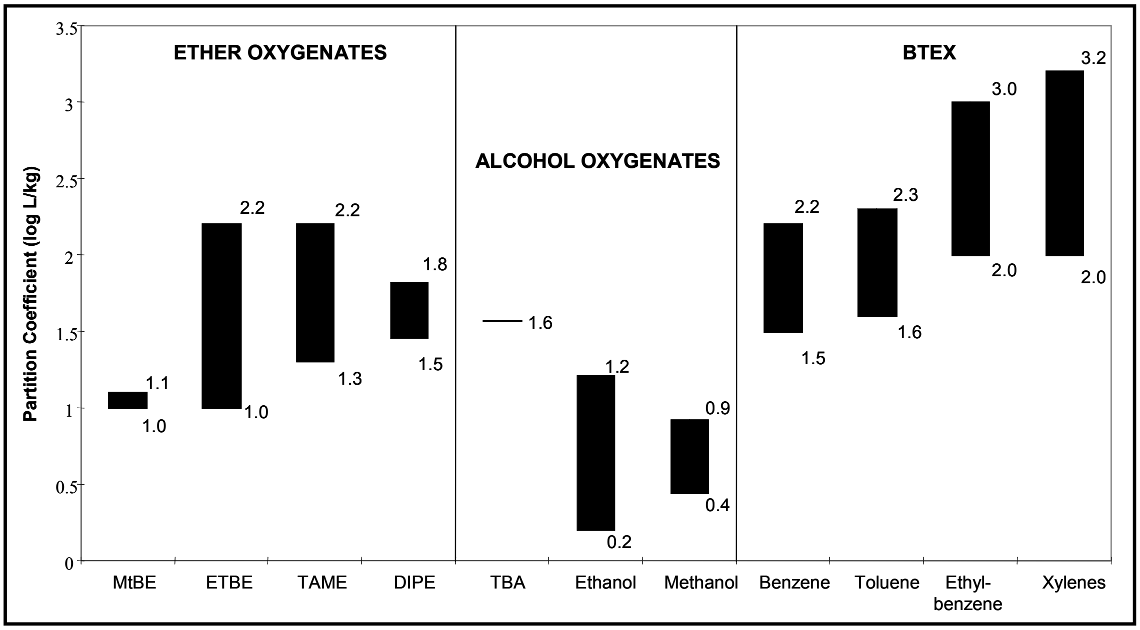
Similar to air sparging, air stripping relies on the volatilization of contaminants from the aqueous to the vapor phase. The property that shows the extent to which this transfer can take place during air sparging is the Henry's Law Constant, which represents the extent to which a contaminant will partition between the dissolved state and the vapor state under equilibrium conditions. A contaminant with a greater Henry's Law Constant is more readily stripped from water during air stripping than one with a lesser Henry's Law Constant. The discussion in Section 4.1.2 related to the affect of the properties of fuel oxygenates on air sparging is also applicable to air stripping. As discussed in that section, all common fuel oxygenates (with the possible exception of DIPE) are less readily stripped than BTEX (based on their Henry's Law Constants). Because of this, air stripping systems designed to treat oxygenates often are designed to allow for more air/water contact time than a system designed to treat BTEX constituents at the same concentrations. This is typically accomplished by use of a larger stripping tower or packing material with a higher specific surface area. As an illustration, based on their ranges of Henry's Law Constants, ether-based oxygenates would require 5 to 10 times more air contact than BTEX to volatilize the same concentration of contaminant. Because of this, an air stripping system designed to treat BTEX may not be capable of adequately addressing ether-based oxygenates. Alcohol-based oxygenates are even more difficult, and in some cases impractical, to strip from groundwater.

The properties of oxygenates may also affect the applicability and design of a system to treat the contaminated vapor effluent resulting from air stripping, if one is required. These affects are discussed in Section 4.2 about SVE.

Adsorption

In adsorption processes, contaminated water is contacted with a solid adsorption media, such as GAC or resin. Based on their equilibrium properties relative to the specific adsorption media, contaminants will partition from the water to the solid until the system has reached equilibrium. The maximum concentration of a given contaminant that can be adsorbed is dependent on the type of adsorption media used, the specific contaminant and its concentration, concentrations of other substances in the water that may competitively adsorb, as well as other parameters such as temperature. Although the actual treatability of a contaminated water stream is dependent on all of these parameters, the relative treatability of MtBE and other oxygenates can be estimated based on their relative tendency to partition from water to an organic matrix. One common measure of this tendency is the organic carbon-based partition coefficient. Generally, contaminants with lower partition coefficients are less amenable to treatment using GAC or resin adsorption. Figure 4.7-1 shows the ranges of partition coefficients for ether- and alcohol based coefficients and BTEX.

Figure 4.7-1. Relative Ranges of Partition Coefficients for Fuels Oxygenates and BTEX



As shown in Figure 4.7-1, the average partition coefficients for ether- and alcohol-based oxygenates are much lower than for BTEX. Based on this, it would be expected that adsorption systems designed only to treat BTEX may not be able to effectively address ether-based oxygenates, and that the lower molecular weight alcohol-based oxygenates would not be amenable to adsorption.

Chemical Oxidation

As discussed in Section 4.5 about *in situ* chemical oxidation, MtBE and other oxygenates are susceptible to degradation through oxidation reactions. If a sufficient amount and strength of oxidant and enough time are provided, all ether- and alcohol-based fuel oxygenates can be destroyed via chemical oxidation. However, the amount and type of oxidant that is necessary for the treatment of MtBE or other oxygenates at a given site will depend on numerous factors beyond the amount of contaminant present. These factors are discussed further in Section 4.5.

There are also technologies that use electrical or other forms of energy to generate oxidizing and reducing radicals in aqueous solution and thereby destroy contaminants such as MtBE and other oxygenates. These technologies include electron beams and ultrasound. High-energy electron beams (E-beams) induce radiolysis (radiation driven splitting) of water to form oxidizing hydroxyl radicals (OH•) as well as reducing hydrated electrons (e_{aq}-) and hydrogen (H•). Ultrasound technology relies on the breakdown of water molecules into oxidizing and reducing free radicals (OH• and H•) under the intense heat and pressures generated during ultrasound-induced cavitation. Both of these technologies have been demonstrated on the pilot scale in application to groundwater contaminated with MtBE (Kelley, Marley, and Sperry, 2003).

Biotreatment

As discussed in Section 4.4 about bioremediation, MtBE and other oxygenates are susceptible to biodegradation. For *in situ* biological treatment, the primary focus is on creating conditions that are conducive (sufficient electron acceptors, nutrients, microbes, and co-metabolite) to stimulate biodegradation. With aboveground biotreatment, the creation of these conditions is simpler because the treatment is occurring in a defined, controlled, and accessible system. However, the relative biodegradability of different contaminants, such as ether- and alcohol-based oxygenates, is an important consideration in the selection and design of a biotreatment component for a pump-and-treat system. These factors are discussed further in Section 4.4.

4.7.3 How are Technologies Used for Above-Ground Treatment of Oxygenates?

One or more above-ground technologies are typically used to treat extracted groundwater before reinjection or discharge to surface water or the sewer. Multiple technologies, or treatment trains, are commonly used at sites contaminated with MtBE and other oxygenates (for example, air stripping followed by GAC polishing). A significant amount of literature (some of which is referenced at the end of this report) has been dedicated to the design of above-ground treatment systems. Some of the key considerations relevant to treatment of MtBE and other oxygenates in extracted groundwater are summarized below (California MtBE Research Partnership, 2000).

Air Stripping

- A typical volumetric ratio of air to water for effective treatment of MtBE is at least 150 to 200 parts air to 1 part water, greater than that required to solely remove BTEX.
- Most states require the capture and treatment of air stripper off gas. Typical off-gas treatment technologies that are applicable to MtBE and other oxygenates are adsorption, thermal treatment, and biotreatment. These technologies are discussed in more detail in Section 4.2 about SVE.

Adsorption

- Because of their water solubility and low partition coefficients, MtBE and other oxygenates are difficult to adsorb on GAC. Other, more preferentially adsorbed, contaminants in groundwater may also reduce the capacity of GAC to remove MtBE and other oxygenates. In some cases, the more absorbable contaminants may even displace MtBE or other oxygenates that are already adsorbed. In addition, natural groundwater constituents, such as iron, manganese, or organic carbon may also consume adsorption capacity. Because of this, two or more GAC beds are often used in series so that contaminant breakthrough can be monitored in the first bed without risking the discharge of contaminants into the effluent.
- Certain types of adsorption media have been shown to preferentially adsorb certain contaminants. For example, research has shown that, in some cases, coconut shell based GAC removes MtBE better than typical coal-based GAC. In addition, synthetic resins have been developed to preferentially adsorb some oxygenates, such as TBA, that are less absorbable by GAC. Often, adsorption processes also take advantage of the biodegradability of MtBE and other oxygenates by promoting bacterial growth on the adsorption media (refer to Section 4.4.3 about use of combined treatment technologies that employ adsorption and biological treatment).

Chemical Oxidation

- For the *ex situ* treatment of groundwater contaminated with MtBE or other oxygenates using chemical oxidation, most systems rely on processes that generate hydroxyl radicals, which are capable of completely oxidizing organic material to primarily carbon dioxide and water. Approaches that have been used to generate hydroxyl radicals for the oxidation of MtBE and other oxygenates include the following. In some cases, the treatment system has been tailored for aboveground application. In other cases (for example, ultrasonic cavitation and electron beam), the technologies have only been used in aboveground treatment systems.
  - Combination of hydrogen peroxide and UV light
  - Combination of hydrogen peroxide and ferrous iron (Fenton's chemistry)
  - Combination of ozone and UV light
  - Combination of ozone and hydrogen peroxide (such as in the HiPOx system)
  - Ultrasonic Cavitation (using high-energy ultrasonic vibrations to generate high temperatures and pressures)
  - Electron Beam (using high energy electrons to split water molecules into free radicals)
- The incomplete oxidation of MtBE and other oxygenates may result in the generation of undesirable intermediate products, such as TBF, TBA, and acetone. The design (oxidant dosage and contact time) should be adequate to achieve complete oxidation or additional treatment processes, such as GAC, may be used to address residual contamination.
- The presence of other oxidant-consuming constituents in the feed water, such as iron, natural organic carbon, carbonates, bromide, and other contaminants, may require pretreatment of the feed stream, additional oxidant dosage, or more contact time to adequately destroy the MtBE and other oxygenates.

Biotreatment

- Biological treatment systems that incorporate mechanisms to retain sufficient biomass generally are applicable to groundwater containing lower concentrations of contaminants. These systems typically consider the limited supply of carbonaceous material (food) to sustain a viable population of degrading microbes. Attached growth bioreactors, and suspended growth bioreactors that incorporate membrane-based biomass separation systems, generally are appropriate for these applications.
- Because the biological degradation rate of MtBE has been observed to be slower than for other common contaminants, such as BTEX, MtBE will typically be the rate-limiting contaminant that determines the necessary hydraulic retention time for a mixed contaminant system, since it will typically be the slowest to degrade (see additional discussion in Section 4.4 about relative rates of biodegradation among oxygenates).
- Due to the difficulties involved in maintaining an adequate microbial mass in application to low concentrations of MtBE or other oxygenates in groundwater, treatability studies are often performed to confirm that extracted groundwater can be adequately treated in a bioreactor.

Recently, some efforts have been made to combine treatment technologies that employ adsorption and biological treatment. Biological treatment technologies that use naturally occurring microorganisms have successfully treated MtBE-contaminated groundwater. However, these microorganisms do not grow efficiently on MtBE, and thus require a microbial retention mechanism. Granular activated carbon (GAC) serves as an attachment media that immobilizes microbes. Other retention mechanisms include permeable barrier membranes and reactive barriers. GAC is often promoted for its adsorption capability of environmental pollutants. However, in the presence of BTEX, the affinity of MtBE and TBA to adsorb to carbon is lowered. Consequently, GAC may not offer substantial adsorption capacity for MTBE or TBA.

More detailed information relevant to the application of above-ground treatment at sites contaminated with fuel oxygenates and in general is available in the following documents:

- Cohen, R.M., J.W. Mercer, and R.M. Greenwald. 1998. *EPA Groundwater Issue, Design Guidelines for Conventional Pump-and-Treat Systems.* EPA 540/S-97/504. September. http://www.epa.gov/ada/issue.html.
- Li, Tie, U. Raaj, P.G. Patel, D.K. Ramsden, and J. Greene. 2003. "Groundwater Recovery and Treatment". In Moyer and Kostecki, Eds. *MtBE Remediation Handbook.* Amherst Scientific Publishers.
- California MtBE Research Partnership. 2000. *Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MtBE) from Drinking Water, Second Edition.* February.

4.7.4 What Projects Have Been Used for Above-Ground Treatment of Extracted Groundwater?

From the 323 projects in the MtBE Treatment Profiles Website dataset, 85 projects were identified where MtBE in groundwater was remediated using pump-and-treat along with 15 additional projects that treated MtBE in drinking water (collectively referred to as pump-and-treat projects). 70 of these projects reported the type of above-ground treatment used, as shown in Table 4.7-1. Short summaries for three demonstration-scale projects of above-ground treatment technologies, *High Biomass Retention Reactor, HiPOx Advanced Oxidation Technology,* and *High Energy Electron Beam*, are included at the end of this section.

Table 4.7-1. Above-Ground Treatment Technologies Used at 70 Groundwater Pump-and-Treat Remediation and Drinking Water Treatment Projects

Aboveground Treatment Technology Employed	# of Pump-and-Treat Projects	# of Drinking Water Treatment Projects	Total # of Projects
Air Stripping Only	8	3	11
Air Stripping with Adsorption	9	1	10
Adsorption Only	18	8	26
Adsorption with Oxidation	1	2	3
Oxidation Only	19	0	19
Biotreatment Only	1	0	1
TOTAL	**56**	**14**	**70**

Notes:

Based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website, as shown in cluin.org/products/mtbe, and summarized in Appendix A. Appendix A shows the specific sites that are summarized here, along with technology design, operation, and performance data for each of the projects.

As shown in the table, the projects in the dataset used adsorption most frequently, either alone or in combination with other technologies. Nine of the 39 projects that used adsorption reported information about the type of adsorption media that was used in the treatment system. Bituminous carbon was used for 4 projects; coconut shell carbon for 2 projects; and, organoclay carbon, resin, or biologically-enhanced GAC were used for one project each. Air stripping (21 projects) and oxidation (22 projects) were also used frequently. Three of the air stripping projects reported that catalytic oxidation was used for off-gas treatment. No other projects reported information about off-gas treatment. Two of the air stripping projects reported air-to-water ratios; they were 150:1 and 200:1. Most (21) of the oxidation projects reported the type of oxidation that was employed. Hydrogen peroxide/ozone was used for 16 projects; hydrogen peroxide/UV was used for 3 projects; hydrogen peroxide alone and ultrasonic cavitation were used for one project each.

As an example of above-ground treatment, a site in Mission Viejo, CA had an operating dual-phase extraction system withdrawing soil vapor and groundwater for treatment with oxidation and bioreaction, respectively. Initially, the major contaminant was TBA, with a lesser concern about MtBE. However, as the formation dried out and more porosity developed, the concentrations of BTEX were found to be climbing. Site consultants considered that if the BTEX exceeded the TBA/MTBE concentration for a long time period, then the bio-mass would prefer the BTEX and would lose its ability to consume TBA/MTBE. To address this concern, a "sacrificial" carbon canister containing 200 pounds of coconut carbon was installed ahead of the bio-reactor to remove the BTEX while allowing the TBA/MTBE to pass through and be remediated in the bio-reactor. While feeding approximately 1.5 gpm of a stream containing approximately equal concentrations of TBA/MTBE and BTEX, the stream exiting the carbon canister showed breakthrough for TBA in two days, the first time a sample was taken. The TBA entering and leaving the carbon canister showed no decrease in concentration after the first week. The BTEX took about 45 days to break through (O'Connell, 2004).

4.7.5 How Has Above-Ground Treatment Performed in Treating Oxygenates?

Of the projects in the database, four completed projects using pump-and-treat provided performance data for initial and final MtBE concentrations. Median concentrations were 27,000 μg/L for before treatment, and less than 1μg/L for after treatment. The median project duration for these projects was 14 months. Note that these treatment performance data are based on the data provided by project managers and others in the source materials used to prepare the treatment profiles website, as summarized in Appendix A. Appendix A shows the specific sites that are summarized here, along with technology design, operation, and performance data for each of the projects. For projects where more than one technology was used, performance data are presented under each of the technologies used for the project.

4.7.6 What Costs Have Been Associated with Using Pump-and-Treat in Treating MtBE?

Project cost data were reported for 12 pump-and-treat projects in the dataset based on type of above-ground treatment used; these include data for both ongoing and completed projects. In most cases, the components that make up the project costs were not reported. However, it is likely that these costs incorporate different components, such as treatment, monitoring, design, oversight, and health & safety. Most of the reported costs were for ongoing projects and represent either a partial actual cost as of the time that the report was made or an estimated total project cost.

Table 4.7-2 summarizes the cost information from these 12 projects, broken down the type of above-ground treatment technologies used.

Table 4.7-2. Cost Summary for Pump-and-Treat – By Aboveground Treatment Type

Aboveground Treatment Technology(ies)	# of Projects	Total Cost Range		Median Total Reported Cost ($)
		Minimum	Maximum	
Air Stripping Only	6	74,000	1,200,000	545,000
Air Stripping with Adsorption	3	216,000	1,180,000	339,000
Adsorption Only	3	160,000	624,000	180,000
TOTAL	12	450,000	3,000,000	1,060,000

Table 4.7-3 summarizes ranges of projected unit costs estimated by the California MtBE Research Partnership for the treatment of different flow rates (60, 600, and 6,000 gallons per minute (gpm) of MtBE-contaminated water using air stripping, oxidation, and adsorption technologies. These results show that air stripping is less costly than either adsorption or oxidation, and that there are economies of scale with treatment of relatively larger quantities of water.

Table 4.7-3. Estimated Range of Unit Costs for Above ground Treatment Technologies

Technology Category	$/1,000 Gallons Treated (60 gpm system)		$/1,000 Gallons Treated (600 gpm system)		$/1,000 Gallons Treated (6,000 gpm system)	
	Minimum	**Maximum**	**Minimum**	**Maximum**	**Minimum**	**Maximum**
Air Stripping	1.66	3.20	0.30	1.09	0.13	0.64
Adsorption	2.30	4.61	0.77	2.37	0.30	2.22
Oxidation	2.18	4.11	0.57	2.08	0.32	1.59

Source: The California MtBE Research Partnership, 2000

4.7.7 What Factors May Affect the Performance and Cost of Above-Ground Treatment for Oxygenates?

Once water contaminated with MtBE or other oxygenates has been extracted, the relative tendency to remain in the aqueous phase can make above-ground treatment more complicated than the treatment of other contaminants, such as BTEX. Key factors that may affect the cost and performance of above-ground treatment include:

- The concentrations of oxygenates and other contaminants
- Extracted groundwater flow rates
- Other groundwater chemistry parameters that may interfere with treatment, such as natural organic carbon, iron, manganese, hardness, alkalinity, pH; effluent water and off-gas discharge standards

These factors may influence the specific above-ground treatment technology that is selected, the possible need for multiple above-ground treatment processes (treatment trains), and the need for pre-treatment of groundwater or post-treatment of off-gas. Also, as with the extraction component, the presence of an active source area may result in the need for long-term operation of above-ground treatment systems.

4.7.8 Conclusions

Based on the information available from the projects listed in the MtBE Treatment Profiles Website dataset and other information contained in the reference documents reviewed in preparation of this report, the following conclusions were identified regarding the use of above-ground treatment for sites contaminated with MtBE and other oxygenates.

Treatability of MtBE and Other Oxygenates Using Above-Ground Treatment

- **Air Stripping** – Treatment of ether-based oxygenates may require greater air to water ratios than treating only BTEX; treatment of alcohol-based oxygenates may be impractical
- **Adsorption** – Ether-based oxygenates are less readily removed than BTEX using GAC and some alcohol-based oxygenates may not be adsorbable at all; synthetic resins that more selectively remove fuel oxygenates are available

- **Chemical Oxidation** – Fuel oxygenates can be destroyed using hydroxyl radical oxidation; oxidant dosage and contact time based more on overall oxidant demand of extracted groundwater than types of oxygenate contaminants
- **Biotreatment** – Fuel oxygenates can be biodegraded given adequate retention time in a bioreactor with a sufficient mass of conditioned microbes
- In general, above-ground treatment systems can be more readily controlled and monitored to optimize the removal of MtBE and other oxygenates than *in situ* treatment systems

Other Potential Limitations to Applying Above-Ground Treatment (EPA, 1995; FRTR, 2002)

- The cost of constructing, operating, and maintaining treatment systems is considered to be relatively high
- Biofouling or mineral precipitation in extraction wells or treatment processes can reduce system performance

4.7.9 Example Projects

The following two project descriptions relate to demonstrations of innovative ex situ treatment systems for groundwater contaminated with MtBE and other oxygenates:

Biodegradation of MtBE in a High Biomass Retention Reactor: Demonstration Study at Pascoag, RI

A pilot-scale specialized Biomass Concentrator Reactor (BCR), an activated sludge type bioreactor that uses a membrane-based biomass separation system, was tested for the aerobic biodegradation of MtBE. The BCR design encompasses an aeration chamber housing a high surface area porous polyethylene membrane system that retains all of the biomass within the aeration chamber. Its simple operation and low maintenance requirements may render it economically more feasible than other water treatment technologies. The water flux through the membrane relies completely on gravity. The system includes 30 membrane compartments, with each one removable for cleaning.

The BCR was used in a demonstration at a Pascoag, RI abandoned gasoline station where substantial amounts of gasoline have leaked into the groundwater, contaminating it with MtBE, TBA, TAME, TAA, DIPE, TBF, acetone, methanol, ethanol, and BTEX. The objective of the study was to demonstrate the effectiveness of the BCR in treating MtBE, other oxygenates, and BTEX to near or below detectable limits. The BCR was operated at the Pascoag site for nearly 6.5 months at up to 5 gpm. Average influent concentrations of volatile organic compounds were: MtBE, 6,500 µg/L; TBA, 69 µg/L; TAME, 1,130 µg/L; TAA, 130 µg/L; DIPE, 36 µg/L; TBF, 29 µg/L; acetone, 480 µg/L; methanol, 300 mg/L; and the sum of BTEX, 3,700 mg/L. Effluent concentrations were very low despite continual flow interruptions from the source wells. Over the entire project, including flow interruptions and non-steady-state flow conditions, MtBE in the effluent averaged near 9 µg/L (< 5 µg/L during 5 gpm steady state flow conditions without flow interruptions), TBA, 0.5 µg/L; TAME, 1.4 µg/L; TAA, ~0.06 µg/L; DIPE, 0.05 µg/L; TBF, 0.02 µg/L; acetone, 6.6 µg/L; methanol, 2 µg/L; and sum of BTEX, 1.3 µg/L. Non-purgeable organic carbon (NPOC) was reduced by close to 50%. A detailed cost analysis has not yet been conducted (Venosa 2003).

Demonstration of the HiPOx Advanced Oxidation Technology for the Treatment of MTBE-Contaminated Groundwater at Port Hueneme, CA

The HiPOx technology is an advanced oxidation process that incorporates high-precision delivery of ozone and hydrogen peroxide to chemically destroy organic contaminants while minimizing bromate formation. A MtBE-contaminated groundwater (initial MtBE concentration of 748 µg/L) from the Ventura County Naval Base in Port Hueneme, CA was used to evaluate this technology. Due to extremely high concentrations of bromide in the feed water (1.3 mg/L) and the desire to limit bromate formation, a pilot-scale system was operated with 630 ozone injector ports in series, as part of EPA's SITE program.

The HiPOx process achieved greater than a 99.87 percent reduction in MTBE concentration and easily met the treatment goal of reducing the concentration of MtBE to below 5 µg/L. However, significant concentrations of MtBE degradation intermediates and oxidation by-products were present in the final effluent. TBA was produced early during the chemical oxidation process. Its concentration was diminished by further oxidation, reaching below its regulatory limit of 12 µg/L in two of the three runs. Acetone was generated and a sizable percentage was left unoxidized in the final effluent (>100 µg/L). Bromate concentrations in the effluent exceeded the drinking water standard of 10 µg/L for all three runs.

A model calculation showed that the HiPOx system may have been fully successful in limiting bromate formation under the chosen oxidant doses if the influent bromide concentration was 0.56 mg/L, or less. Since a bromide concentration of 0.56 mg/L is still extremely high for a drinking water source, the HiPOx system appears to hold promise for destroying MTBE and its oxidative byproduct TBA while controlling bromate formation, even in waters that have high bromide concentrations (Speth and Swanson 2002).

Application of High Energy Electron Beam (E-Beam) to the Treatment of MtBE-contaminated Groundwater at Port Hueneme, CA

A demonstration of the high-energy electron injection (E-Beam) technology in application to groundwater contaminated with MtBE and with BTEX was conducted at the Naval Base Ventura County, Port Hueneme, CA, as part of EPA's SITE program. The E-beam technology destroys organic contaminants in groundwater through irradiation with a beam of high-energy electrons; the oxidizing radicals that are generated by the E-beam react with and destroy organic contaminants, including MtBE and its breakdown products.

Results of two weeks of steady state operation at an E-beam dose of 1,200 kilorads (krads) indicated that MtBE and BTEX concentrations in the effluent were reduced by greater than 99.9 percent from influent concentrations that averaged over 1,700 µg/L MtBE and 2,800 µg/L BTEX. Further, the treatment goals for the demonstration, which were based on drinking water regulatory criteria, were met for all contaminants except for TBA, a degradation product of MtBE. Dose experiments indicated that TBA was not consistently reduced to below the treatment goal of 12 µg/L although the results indicated that tBA by-product formation decreased as dose increased. Acetone and formaldehyde were the two most prevalent organic by-products that were formed by E-beam treatment, with mean effluent concentrations during the two-week steady state testing of 160 and 125 µg/L, respectively. Bromate was not formed during E-beam treatment.

An economic analysis of the E-beam treatment system indicated that the primary costs are for the E-beam equipment and for electrical energy. The estimated cost ranged from over $40 per 1000 gallons for a small-scale remedial application to about $1.00 per 1000 gallons for a larger-scale drinking water application (Venosa and Swanson 2002).

4.8 Other Treatment Technologies: Phytoremediation, PRBs, and Thermal Treatment

Overview

- Other technologies that have been used to treat MtBE and other oxygenates include:
    - Phytoremediation (8 projects in dataset)
    - Permeable Reactive Barriers
    - Thermal Treatment

4.8.1 What Other Technologies are used to Treat MtBE and Other Oxygenates?

In addition to the technologies discussed earlier in this chapter, three additional technologies (phytoremediation, PRBs, and thermal treatment) have also been used to treat MtBE and other oxygenates in soil and groundwater. Phytoremediation is a category of treatment technologies that employ plants (or in some cases fungi) to conduct remediation. Treatment during phytoremediation can be accomplished through one or more natural processes, including enhanced bioremediation in the rhizosphere (plant root zone), phyto-stabilization of contaminants by organic plant material, plant uptake, plant metabolism, and phytovolatilization (volatilization through plant leaves) (EPA, 2000g). PRBs are subsurface barriers that remediate groundwater as it passes through an engineered treatment zone. For the treatment of MtBE and other oxygenates, treatment zones that use bioremediation processes are most common (EPA, 2002e). Thermal treatment is a generic term that applies to technologies that use heat to mobilize, extract, or destroy contaminants either *in situ* or *ex situ*. While these technologies were applied less frequently, they may represent viable treatment options at some sites contaminated with MtBE and other oxygenates.

4.8.2 How Is Phytoremediation Used in Treatment of Oxygenates?

Properties --

Phytoremediation, as it applies to MtBE and other oxygenates, is a relatively new remedial approach and many of the removal and degradation pathways are currently being studied. However, it is known that phytoremediation relies on multiple processes to accomplish the removal of contaminants from shallow groundwater. Each of these processes is affected by different chemical properties as well as site-specific conditions. The biodegradability of oxygenates affects their treatment in the rhizosphere, where the conditions support an abundance of metabolically-active bacteria and fungi that may enhance contaminant degradation. The relatively high solubility and low organic partition coefficients (discussed earlier in this section) of oxygenates generally limits significant removal through phyto-stabilization, but facilitates removal through root uptake. In addition, volatility and Henry's Constants may affect the removal through phytovolatilization (Chard and others, 2001).

Application –

The manner that phytoremediation can be applied to treat MtBE and other fuel oxygenates is highly variable, based on the site conditions, specific contaminants to be treated, cleanup goals, and other factors. Information relevant to the application of phytoremediation at sites contaminated with MtBE and other oxygenates is available in the documents:

- EPA. 2000. Introduction to Phytoremediation. Office of Research and Development. EPA 600-R-99-107. February.

- Chard, J., A.M. Ferro, and J. Greene. 2001. "Recent Advances in Phytoremediation of MtBE Groundwater Plumes". *Contaminated Soil, Sediment, and Water.* Spring.

- Landmeyer, J. E., D. A. Vrblosky and P. M. Bradley. 2000. "MtBE and BTEX in Trees above Contaminated Groundwater". Battelle International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA.

- Newman, Lee and Charles Arnold. 2003. "Phytoremediation of MTBE – A Review of the State of the Technology". In Moyer and Kostecki, Eds. *MtBE Remediation Handbook.* Amherst Scientific Publishers.

- Rubin, E. and A. Ramaswami. 2001. "The Potential for Phytoremediation of MtBE". *Water Res*. 35(5): 1348-1353.

Projects –

From the 323 MtBE treatment profiles, 8 projects were identified where MtBE was treated using phytoremediation. These projects used various approaches, including hybrid poplar trees, Monterey pine, oak, eucalyptus, and engineered wetlands.

Table 4.8-1 summarizes the scale and operational status for the 8 projects in the dataset that used phytoremediation. The data used to compile this information was current at the time the profile for each project was completed. Further information about these projects is provided in Appendix A, including available performance data.

Table 4.8-1. General Information on 8 Projects Using Phytoremediation

Technology	# of Projects	Operational Status		Scale		
		Completed	Ongoing	Bench	Pilot	Full
Phytoremediation	8	5	3	3	4	1

Costs –

No total project cost data were reported for any of the projects in the dataset that employed phytoremediation technology.

4.8.3 How Are PRBs Used in Treatment of Oxygenates?

Properties --

A PRB is a treatment system configuration with treatment zones that can employ any of a number of treatment technologies, such as *in situ* bioremediation or *in situ* chemical oxidation. Depending on which treatment technology is employed, the properties of MtBE and other oxygenates as they apply to that specific technology (as discussed earlier in this section) will affect treatment differently.

Application –

Information relevant to the application of PRBs at sites contaminated with MtBE and other oxygenates is available in the documents:

- Gavaskar, A., N. Gupta, B. Sass, R. Janosy, and J. Hicks. 2000. *Design Guidance for Application of Permeable Reactive Barriers for Groundwater Remediation*. Prepared for U.S. Air Force, Air Force Research Laboratory. March.
- ITRC. 1999. *Regulatory Guidance for Permeable Reactive Barriers Designed to Remediate Chlorinated Solvents.* December.
- EPA. 1998. *Permeable Reactive Barrier Technologies for Contaminant Remediation*. EPA/600/R-98/125. Office of Research and Development. September.
- EPA. 2002. *Field Applications of In Situ Remediation Technologies: Permeable Reactive Barriers*. Office of Solid Waste and Emergency Response. January.
- EPA. 2002. *Economic Analysis of the Implementation of Permeable Reactive Barriers for Remediation of Contaminated Ground Water*. EPA/600/R-02/034. National Risk Management Research Laboratory, Ada, Oklahoma. June.

Projects –

While no projects in the dataset were identified explicitly as using PRBs, several projects discussed under other technologies involved these types of components. For example, several bioremediation projects, such as at Port Hueneme, were performed using a PRB configuration; these are discussed further in Section 4.4.

Costs –

No total project cost data were reported for any of the projects in the dataset that employed *in situ* thermal treatment technology. However, additional information in the literature includes information about the application of PRBs for the treatment of other contaminants. One reference showed a range of total costs for 16 PRB projects ranging from $43,000 to $1,900,000 with a median total cost of $680,000 (EPA, 2000c).

4.8.4 How Is *In Situ* Thermal Treatment Used for Remediation of Oxygenates?

Properties --

Thermal treatment can be used to mobilize or destroy MtBE and other oxygenates from soil either *in situ* or *ex situ*, similar to other petroleum contaminants. Projects in the dataset applied *in situ* thermal treatment. Volatilization from soil is affected by vapor pressure, with a higher vapor pressure making volatilization occur more readily. In general, alcohol-based oxygenates have lower vapor pressures than ether-based oxygenates, but the vapor pressures of both are comparable to or greater than other petroleum contaminants such as benzene. Similar to other organic contaminants, MtBE and other oxygenates may also be susceptible to thermal destruction at high temperatures.

Application –

Information relevant to the application of *in situ* thermal treatment at sites contaminated with MtBE and other oxygenates is available in the following document:

- EPA. 2004. *In Situ* Thermal Treatment of Chlorinated Solvents: Fundamentals and Field Applications. EPA 542-R-04-010. Office of Solid Waste and Emergency Response. March.

Projects –

While no projects in the dataset were identified explicitly as using *in situ* thermal treatment, several projects discussed under other technologies involved these types of components. For example, one site in Texas also discussed under bioremediation (Rural Area Disposal Area, Liberty, TX) used a combination of technologies that included an *in situ* thermal treatment component.

Costs –

No total project cost data were reported for any of the projects in the dataset that employed *in situ* thermal treatment technology.

4.8.5 What Factors may Affect the Performance and Cost of Phytoremediation, PRBs, or Thermal Treatment?

When MtBE or other oxygenates are present and must be remediated at a site, phytoremediation, PRBs, or *in situ* thermal treatment, may be part of a suitable remediation approach. Information about the factors that influence the performance and cost of these systems in general is available in the references listed in this report.

4.8.6 Conclusions

Data from MtBE Treatment Profiles Reporting About Other Treatment Technologies

- Phytoremediation, PRBs, and thermal treatment have been used to remediate groundwater contaminated with MtBE, but less frequently than some other technologies such as air sparging and bioremediation; phytoremediation has been used at 8 sites for MtBE
- All PRB projects in the dataset have treatment zones that employed bioremediation technology
- The thermal treatment projects in the dataset used thermal desorption in conjunction with other technologies, such as *in situ* bioremediation
- No information on total project cost was reported for projects using phytoremediation, PRBs, or thermal treatment

Treatability of MtBE and Other Oxygenates Using Other Treatment Technologies

- Treatability during phytoremediation based on multiple contaminant properties, including biodegradability, solubility, partition coefficient, vapor pressure, and Henry's Constant
- Treatability using PRBs dependant on reactive treatment zone employed
- Vapor pressure from soil affects volatilization during thermal treatment; generally oxygenates have comparable or higher (more favorable for volatilization) vapor pressures than other petroleum contaminants

Other Potential Advantages of Applying Other Treatment Technologies

- Phytoremediation or PRBs may be a cost-effective alternative for remediating or containing relatively low concentration, shallow, and widespread groundwater plumes
- Thermal treatment technologies tend to remove oxygenates along with other petroleum contaminants (such as petroleum hydrocarbons) that are more typically treated using this technology

Other Potential Limitations to Applying Other Treatment Technologies

- The processes that effectively treat MtBE and other oxygenates during phytoremediation are still being studied
- Phytoremediation may be less applicable to higher concentration or deeper groundwater plumes

5.0 NON-TREATMENT REMEDIES

Overview

- Non-treatment remedies that address oxygenates include excavation, free product recovery, MNA, and institutional controls
- Non-treatment remedies may be appropriate for use either alone or in conjunction with one or more of the other remedies discussed in this report
- Containment (caps or vertical barrier walls) typically have not been used at sites contaminated with MtBE, and is not discussed further

While this report focuses on treatment technologies that have been used for MtBE and other fuel oxygenates, many sites are being remedied using non-treatment options that include excavation, free product recovery, MNA, and institutional controls. In addition, these remedies sometimes are used in conjunction with one or more of the treatment technologies discussed in Section 4.

5.1 Excavation

Excavation is the removal of contaminated soil or sludge from a site by use of mechanical equipment. It often is used at sites where significant volumes of petroleum products are present in the soils located near the surface, and which are likely to be a continuing source of contaminant migration. Commonly, excavation is performed prior to or while implementing other remedies such as groundwater treatment technologies. Similar to free product recovery, excavation is used to remove/control the source of contamination, so that MtBE will not continue to migrate to the vadose zone and groundwater (FRTR, 2002).

Site-specific characteristics, such as the presence of aboveground and below ground obstructions, largely dictate the implementation of excavation. Locations where underground utilities or storage facilities exist may require extensive and time-consuming exploratory excavation and hand-digging. Excavation around or near buildings may require the use of underpinning or sheet piling to stabilize the structure and rerouting of utility lines. Shoring or sloping may be required in sandy soil to maintain trench wall stability. Monitoring for air quality may be required during excavation. When fugitive air emissions exceed air quality standards, there may be limitations imposed on the quantity of soil that can be excavated per day.

Excavation equipment ranges from hand tools, such as pick axes and shovels, to backhoes, front-end loaders, clamshells, and draglines, depending on the amount of soil to be excavated, the total depth of the excavation, moisture content of the soil, and the space allowed at the site for staging of excavated material. Backhoes and front-end loaders are the most commonly used equipment for excavation of relatively shallow (less than 15 ft bgs) soils. Excavation rates for these types of units with 1 cubic yard bucket capacities are typically 75 cubic yards per hour. Larger bucket capacities can increase this rate to up to 160 cubic yards per hour (ECHOS, 2002). The maximum excavation rate using hand tools is approximately 1 cubic yard per hour /laborer.

Factors that affect the costs for excavation include the depth of contamination, depth of groundwater (requiring dewatering), and extent of underground infrastructure and/or nearby structures that require shoring. The cost for excavation tends to be higher for areas with deeper contamination, shallower groundwater, and more infrastructure and nearby structures.

5.2 Free Product Recovery

Free product recovery is the extraction of separate phase material (primarily petroleum liquids) that is located in the subsurface (in the case of petroleum liquids, at the top of the water table). It is often used at sites where significant volumes of petroleum products have reached the water table, and which are likely to be a continuing source of contaminants migrating to the vadose zone or dissolving in groundwater. Commonly, free product recovery is performed prior to or during implementation of remedies such as groundwater treatment. Similar to excavation, free product recovery is used to remove/control the source of contamination, so that the source will not continue to migrate to the vadose zone or the groundwater.

Note that free product removal is a Federal regulatory requirement, under 40 CFR Section 280.64. This section requires owners and operators to remove free product to the maximum extent practicable, while continuing other remedial actions, as discussed in that section.

Technologies typically used to recover free product include skimming equipment in wells, trenches, or excavation pits, and pumping of free product. These approaches have been used with and without depressing the water table to enhance migration of free product to a well or drain. The design of a free product recovery system requires an understanding of the site hydrogeology and characteristics, the types, extent, and distribution of free product in the subsurface, and the engineering aspects of the equipment and installation. Free product recovery sometimes is combined with other technologies to enhance removal of contaminants from the vadose zone or that are dissolved in the groundwater.

EPA published a guide for state regulators about how to effectively recover free product at leaking USTs, *How to Effectively Recover Free Product at Leaking Underground Storage Tank Sites; A Guide for State Regulators* (EPA, 1996). In that guide, EPA provided scientific and engineering considerations for evaluating technologies for the recovery of free product from the subsurface. The guide discussed the behavior of hydrocarbons in the subsurface, methods for evaluating recoverability of subsurface hydrocarbons, and recovery systems and equipment.

5.3 Monitored Natural Attenuation

EPA defines MNA as “the reliance on natural processes, within the context of a carefully controlled and monitored site cleanup 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 processes include biodegradation, dispersion, dilution, sorption, volatilization, stabilization, and transformation. These processes reduce site risk by transforming contaminants to less toxic forms, reducing contaminant concentrations, and reducing contaminant mobility and bioavailability”. Other terms for natural attenuation in the literature include “intrinsic remediation”, “intrinsic bioremediation”, “passive bioremediation”, “natural recovery”, and “natural assimilation” (EPA, 1999b).

While offering the potential to cleanup sites at lower cost, MNA typically would require a longer period of time to achieve remediation objectives, compared to active remediation measures. In addition, it generally requires extensive long-term monitoring data. Other potential limitations of MNA include the potential that the toxicity and/or mobility of transformation products may be greater than for the parent compound (e.g., TBA as a degradation product of MtBE); hydrologic and geochemical conditions amenable to natural attenuation may change over time and could result in renewed mobility of previously-stabilized contaminants; and more extensive education and outreach efforts may be required to gain public acceptance of MNA. Information about research into field use of MNA is provided in Schirmer 1999.

EPA published a guide about the steps needed to understand the rate and extent to which natural processes are reducing contaminant concentrations, *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (EPA, 1998b). While this guide is directed at sites contaminated by chlorinated solvents, some of the steps would also have relevance for sites contaminated by oxygenates like MtBE. The guide identifies parameters that are useful in the evaluation of natural attenuation and provides recommendations on how to analyze and interpret the data collected from the site characterization process. It also provides suggestions for integrating MNA into an integrated approach to remediation that includes an active remedy.

Recently, EPA published a report titled "Performance Monitoring of MNA Remedies for VOCs in Ground Water" (EPA, 2004a) that provides guidance about types of monitoring used during MNA remedies.

5.4 Institutional Controls

ICs are non-engineered instruments such as administrative and/or legal controls that minimize the potential for human exposure to contamination by limiting land or resource use, and generally are used in conjunction with engineering measures such as treatment or containment. ICs are used during all stages of a cleanup and often involve multiple activities (“layered IC”) implemented in parallel or in series. Examples of ICs are easements, covenants, well drilling prohibitions, zoning restrictions, and special building permit requirements (sometimes referred to as deed restrictions) (EPA, 2000d).

Often, ICs are considered within the context of long-term plume management and MNA. Typically, after the source of contamination has been addressed (such as through removal or destruction), ICs are used to limit the long-term use of a site and the potential for exposure of residual contaminants to human or environmental receptors. When deciding about appropriate types of ICs, site managers look at the life-cycle strengths, weaknesses, and costs for implementation, monitoring, and enforcement, and coordination with state and local governments that have responsibilities for ICs. Additional information about ICs is available in *Institutional Controls: A Site Manager’s Guide to Identifying, Evaluating, and Selecting Institutional Controls at Superfund and RCRA Corrective Action Clean-ups* (EPA, 2000d).

6.0 REFERENCES

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APPENDIX A
MtBE TREATMENT PROFILE DATA

(see www.cluin.org/mtbe)

Office of Solid Waste
and Emergency Response
(5102G)

EPA 542-R-04-009
May 2004
www.epa.gov/tio
www.cluin.org/mtbe

Official Business
Penalty for Private Use $300