



# Research Strategy for Oxygenates in Water

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Office of Research and Development  
U.S. Environmental Protection Agency  
Washington, DC 20460

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## Preface

The purpose of this document is to identify key issues related to assessing and managing the potential health and environmental risks of oxygenate contamination of water. Oxygenates are chemicals added to fuels (“oxyfuels”) to increase the oxygen content and thereby reduce certain emissions from use of the fuel. This research strategy builds on and extends an earlier document, *Oxyfuels Information Needs* (U.S. Environmental Protection Agency, 1996), which included water issues but tended to focus more on inhalation health risk issues. As a research strategy, the present document focuses on those gaps and limitations in current information that constitute the most critical and immediate needs to be addressed in support of risk assessment and risk management efforts. The document is primarily intended to serve as a starting point and general guide to planning needed research. It is not a comprehensive review of issues related to oxygenates in water, nor does it attempt to lay out in detail the specific studies and projects that may be needed.

Efforts to address many of the needs identified in this document have already begun or are under consideration by various organizations. A current listing of such projects may be found in Appendix 2, *Current Projects Related to Oxygenates in Water*.

Anyone who wishes to comment on this document should do so in writing by July 31, 1998, submitting their comments to Dr. J. Michael Davis, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

# 1. INTRODUCTION

The contamination of ground and surface waters by motor vehicle fuels and fuel additives is not a new problem, given the history and pervasive use of fuels in the 20th century. Well over a million underground fuel storage tanks exist in the United States, and leaks from these tanks have been the focus of major programs to prevent or clean up such releases. Transport of fuels via pipelines and in bulk containers also presents the potential for accidental releases and consequent environmental contamination. Experience suggests that contamination from these and other sources of fuel releases can affect water quality and the biota that depend upon the water, including human populations that may use the contaminated water.

Against this background of experience with fuel-related contamination of ground and surface waters, recent events have focused attention on what appear to be somewhat different characteristics associated with fuels containing chemicals known as oxygenates. Oxygenates are added to fuel to increase its oxygen content and thereby reduce certain emissions from use of the fuel. Of the several ethers and alcohols that may serve as oxygenates, methyl tertiary butyl ether (MTBE) is the most commonly used. Monitoring of groundwater quality by the U.S. Geological Survey (USGS) indicates that MTBE has become detectable in shallow groundwater samples in certain urban areas in recent years, with concentrations ranging from below the reporting level of 0.2 µg/L to over 20,000 µg/L (Squillace et al., 1996). Reports of point-source MTBE contamination of drinking water sources at well over 100 µg/L, including aquifers serving as the primary source of drinking water for the city of Santa Monica, CA (California Department of Health Services, 1998), raise several important questions about potential environmental and public health impacts of oxygenated fuels.

A key question is whether oxygenates in water pose a significant threat to human health or the environment. To assess the risks of MTBE or any other oxygenate, the potential for exposure to, and effects of, the contaminant(s) in question must be characterized. At present, however, only limited information exists for characterizing the possible risks of oxygenates in water. For example, the extent of population exposures to MTBE in drinking water is unknown. Even in cases where MTBE is clearly present in public or private water supplies, limited guidance exists as to the levels that would be acceptable or unacceptable from the standpoint of public health or

consumer acceptability. The U.S. Environmental Protection Agency (EPA) Office of Water recently released a Drinking Water Advisory for MTBE (U.S. Environmental Protection Agency, 1997a). As the full title of the document indicates, it provides “Consumer Acceptability Advice and Health Effects Analysis on [MTBE].” The Advisory “recommends that keeping levels of contamination in the range of 20 to 40 µg/L or below to protect consumer acceptance of the water resource would also provide a large margin of exposure (safety) from toxic effects.” However, the document discusses “many uncertainties and limitations associated with the toxicity data base for this chemical” and notes the consequent difficulty in estimating a risk level for this contaminant in drinking water. The uncertainties in assessing the health risks of MTBE are reflected somewhat in the various guidance values (e.g., advisories, action levels, standards) that have been issued by individual states, ranging from 35 µg/L in California to 230 µg/L in Illinois (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). As efforts to assess health risks and derive guidance values continue at the local, state, and federal levels, the need for an adequate scientific foundation for these efforts intensifies. Without more definitive scientific information, uncertainties will continue to dominate risk assessments of oxygenates.

If it is concluded that a risk or problem exists, other questions arise in formulating actions that might be taken to address oxygenate contamination of water. For example, what are the sources of contamination, how long is the contamination likely to persist, how widespread might the contamination be, what cost-effective technological methods exist to remove the contaminant(s) from water, how can further contamination be avoided, and a host of other questions face risk managers. A recent review of fuel oxygenates and water quality (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) notes that for various reasons, including the potentially greater persistence of MTBE in ground water than other components of gasoline, remediation of MTBE-contaminated ground water may pose unique problems. The Interagency Assessment also notes the possibility that ground water could be contaminated by deposition of oxygenates from the ambient atmosphere. A quantitative answer to the question of whether non-point sources or point sources, such as leaking underground storage tanks, pose a greater potential risk of environmental contamination is not available at present.

Risk assessment and risk management require information that is generally obtained through research, data collection, or analysis of data that already exist. The purpose of this document is to identify the key limitations in current information needed to assess and manage the

potential health and environmental risks related to oxygenates in water. This research strategy builds on and extends an earlier document, *Oxyfuels Information Needs* (U.S. Environmental Protection Agency, 1996), which encompassed water issues but tended to emphasize inhalation health risk issues. As noted in *Oxyfuels Information Needs*, the benefits and risks of any given oxygenate must be assessed in relation to an alternative, such as conventional gasoline. A full comparative assessment of this type is obviously a complex, multifaceted endeavor (see U.S. Environmental Protection Agency, 1992a). The present research strategy is much more limited in scope. By focusing on only the key information required to support the most pressing risk assessment and risk management needs, it is hoped that progress will be achieved more readily than by attempting to cover every possible issue in a comprehensive manner.

This strategy document is primarily intended to serve as a starting point and general guide to planning research related to oxygenates in water; it does not attempt to lay out in detail the specific studies and projects that may be needed. Nor is this document a formal assessment of environmental or health risks associated with oxygenates or an in-depth analysis of candidate risk management options for addressing this problem. The reader may wish to consult other reports for more detailed reviews of available information on the health and environmental effects of oxygenates (e.g., U.S. Environmental Protection Agency, 1993, 1994; Health Effects Institute, 1996; Interagency Oxygenated Fuels Assessment Steering Committee, 1996, 1997; National Research Council, 1996), especially the “Water Quality” chapter from the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). Note that all of these reports have pointed out the lack of adequate information by which to assess fully and definitively the risks and benefits associated with oxyfuels in comparison to conventional fuels.

Some brief background information on why fuel oxygenates are used may be useful. The 1990 Clean Air Act Amendments (CAAA) created two fuel programs to be administered by EPA that require the use of oxygenates (U.S. Code, 1990). The first program began in the fall of 1992 with the objective of reducing carbon monoxide (CO) emissions in several areas of the country where the National Ambient Air Quality Standard (NAAQS) for CO was exceeded. Under this program, the CAAA required the sale of gasoline with an oxygen content of 2.7% by weight during the winter or cold weather season in designated areas that failed to attain the NAAQS for CO. The second program required the year-round use of reformulated gasoline (RFG) containing

2.0% oxygen by weight, beginning in 1995, in selected areas having the highest levels of tropospheric ozone. In addition to reducing emissions of ozone precursors, the RFG program was also intended to help reduce the emissions of certain toxic organic air pollutants. Collectively, cold-weather oxygenated gasoline and year-round RFG with oxygenate may be referred to as “oxyfuels.”

Although MTBE and, to a lesser extent, ethanol (EtOH) currently dominate the marketplace, no specific oxygenate is required or designated by the 1990 CAAA. Several other ethers and alcohols may also serve as oxygenates and could become more prevalent, depending on various factors such as cost, ease of production and transfer, and blending characteristics. These oxygenates include ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), tertiary amyl ethyl ether (TAEE), diisopropyl ether (DIPE), dimethyl ether (DME), and tertiary butanol (TBA). The chemical properties of several oxygenates are listed in Appendix 1. To achieve the specified oxygen content requirements, approximately 15%-vol MTBE or 7.5%-vol EtOH can be used to yield the 2.7%-wt oxygen for the winter fuel program and approximately 11%-vol MTBE or 5.5%-vol EtOH for the 2.0%-wt oxygen required by the RFG fuel program.

According to EPA’s Office of Mobile Sources, about 30% of U.S. gasoline currently contains some form of oxygenate for air quality improvement purposes. Beginning in the late 1970s, MTBE and EtOH were used to increase the octane value of gasoline in the United States as lead was phased out. Roughly 25% or more of U.S. fuel has contained MTBE or EtOH as an octane-enhancer in a given year, but the current usage of MTBE for octane is considerably lower, constituting perhaps 3 to 5% of the fuel supply (Kneiss, personal communication). These levels of usage are subject to alteration as economic variables (e.g., the price of crude oil) and other factors change. The concentration of MTBE used for octane purposes in conventional gasoline may vary widely up to an allowable limit of 15%-vol MTBE, depending on other constituents and properties of the fuel, but probably is more typically on the order of 1 to 8%-vol MTBE. Gasoline containing 10% EtOH, often referred to as “gasohol,” represents about 10% of all gasoline sold in the United States, but may be much more prevalent in certain locales, particularly in the Midwest. Approximately 21 billion kg MTBE was used in U.S. gasoline in 1995, and fuel ethanol use was about 3.8 billion kg (U.S. Department of Energy, 1995a,b).

This document applies to all ether and alcohol oxygenates unless otherwise stated. It tends to refer more to MTBE in part because of its predominant use and in part because more

information is generally available for MTBE than for the other ethers and alcohols (except perhaps for EtOH). Nevertheless, it should not be inferred that the only oxygenate warranting attention is MTBE.

This research strategy is organized around the following headings:

- Source Characterization
- Transport
- Transformation
- Occurrence
- Exposure
- Aquatic Toxicity
- Health Effects
- Release Prevention
- Contaminant Removal

Within each of these areas, a brief background section highlights currently available information on key issues, followed by a section that identifies research or other information gaps that emerge as needs. Note that the grouping of topics is somewhat arbitrary. The overlap in various areas should be seen as a potential benefit in terms of combining objectives and resources for projects that can be feasibly and appropriately linked. Such leveraging of resources could extend across organizational boundaries as well.

## **2. SOURCE CHARACTERIZATION**

### **2.1 Background**

Releases of fuel oxygenates occur during manufacture, distribution, storage, and use, particularly from point sources such as underground storage tanks (USTs), pipelines, and refueling facilities. The Toxics Release Inventory (TRI) estimates that MTBE production releases in the United States amounted to approximately 3.3 million lb (1.5 million kg) in 1994. Of this total, about 97% was released to the air and less than 3% was discharged to surface water. For mobile sources, assuming an estimated consumption of 21 billion kg MTBE in 1995 (based on imported as well as domestic production volumes, U.S. Department of Energy, 1995a,b), and an

average U.S. corporate fleet emission rate of approximately 3.8 mg MTBE per gram MTBE in fuels (Wyborny, 1997), total motor vehicle emissions of MTBE in 1995 are estimated to have been on the order of 80 million kg in the United States.

Impacts to water resources can be loosely grouped into two categories: (1) widespread impacts occurring at low concentrations and (2) local impacts occurring at high concentrations. The first group is often the result of indirect sources, such as rainfall that is in contact with air contaminated by oxygenates as a result of air emissions from vehicles and infiltrates to ground water, and may be spread over large areas. Also, leakage from motorized recreational water craft can be considered a diffuse source of contamination of surface water bodies such as reservoirs. The second category results from direct releases to surface and ground water from such sources as leaking USTs, pipelines, or tank cars.

Oxygenates in the atmosphere degrade with a half-life as short as 3 days (Smith et al., 1991; Wallington et al., 1988). However, MTBE is soluble in water and, because of its relatively low Henry's Law constant, partitions readily from air to rainfall and snowfall. The concentration in precipitation is determined primarily by the concentration in the atmosphere, the Henry's Law constant at a given air temperature, the time that the precipitation is exposed to the MTBE, and other characteristics of the precipitation that determine contact efficiency, e.g., rain droplet size and snow flake surface area (Hoff et al., 1998). This process could result in deposition to land surface and subsequent contamination of surface and ground water. The detection of MTBE in about 41 (7%) of 592 stormwater samples collected in 16 cities and metropolitan areas from 1991 to 1995, with the highest percentage of detections found in samples collected during high MTBE usage winter months (Delzer et al., 1996), is consistent with atmospheric washout of MTBE in rain or snow to the ground surface. Measured concentrations of MTBE in the stormwater samples ranged from 0.2 to 8.7 ppb, with a median of 1.5 ppb. It is possible that MTBE could accumulate in snow at sites such as service stations, parking lots, and city streets and be released as a pulse source to soil or ground water as the snow melts. Modeling calculations have predicted MTBE concentrations in rainwater ranging from <1 ppb to 3 ppb, within the range of concentrations actually found in groundwater samples (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). The use of shallow ground water for public and private water supplies makes such nonpoint contamination a potential public health issue as well as an environmental quality issue.

Direct releases of MTBE and other fuel oxygenates to surface and groundwater sources of drinking water also occur. The majority of direct releases of MTBE to surface water reported to TRI were attributable to only a few petroleum product facilities. Refueling and operation of boats and other recreational water craft are also suspected as significant sources of releases of MTBE to surface waters in heavily used recreational areas. Detections of MTBE in some drinking water reservoirs in California have prompted studies on the input of MTBE to surface waters via recreational watercraft, precipitation, and snowmelt runoff (e.g., Reuter, 1997; Dale et al., 1997). Other possible sources of MTBE to surface water could include water released from wastewater treatment operations at petroleum operations and publicly owned treatment works.

Releases from leaking USTs are believed to be the primary source of localized releases of MTBE in high concentrations. According to EPA's Office of Underground Storage Tanks (OUST), nearly 1 million federally regulated USTs are currently in use at approximately 360,000 facilities in the United States. Not all of these USTs contain oxyfuels or gasoline with MTBE or EtOH as octane enhancers, but it has been estimated that roughly 50% of the gasoline sold in the United States in recent years has contained MTBE or EtOH (Kneiss, personal communication). Some of the earliest documented UST releases involving MTBE occurred in Maine in the mid-1980s (Garrett, 1987). More recently, drinking water wells in Santa Monica were shut down because of MTBE contamination due, it is believed, to one or more leaking USTs (Geraghty & Miller, Incorporated, 1996). Since 1988, 330,000 confirmed releases from regulated USTs have been reported to EPA/OUST. Based on historical trends, OUST estimates that 100,000 further releases will be reported in the next few years as existing USTs are upgraded, closed, or replaced. This estimate does not include an even greater number of federally unregulated storage tanks. Although EPA regulations (§280.21, Code of Federal Regulations, 1990) require that all USTs be upgraded, closed, or replaced by December 1998, current estimates indicate that 25 to 35% of USTs will not be in compliance by that date.

Despite recent and ongoing studies, it is not clear whether the greater impact from MTBE or other fuel oxygenates to ground water is from diffuse or point sources (i.e., what fraction of the MTBE or other oxygenate load and exposure is diffuse [e.g., from precipitation] or is related specifically to spills or leaks from fuel containers). Although relatively high groundwater concentrations may be readily associated with point source releases, concentrations on the order

of 10 ppb or lower could be associated with nonpoint sources as well as point sources (Interagency Assessment Committee, 1997).

## 2.2 Needs

A model linking air to land to surface water and ground water fate for oxygenates needs to be developed and tested. Such an airshed-watershed model could be used to conduct ecosystem exposure assessments, serve as a key input to human exposure assessments, design management and remediation strategies, and assist in source identification and apportionment. In particular, the model could be used to predict upper limit values of surface and ground water concentrations from ambient sources that could be compared to measured values, such as those expected from the ongoing USGS study at Glassboro, NJ (Baehr and Ayers, 1997). A recent review of the environmental behavior and fate of MTBE by Squillace et al. (1997) summarizes important transport and fate processes and could provide a starting point for the development of such a model. The model could also be used to estimate snow blanket buildup of oxygenates and subsequent release at first thaw. These model results could then be compared to data from field studies designed to test this potential pulse loading mechanism in a watershed. Once this modeling tool is developed and tested, it could be used to provide a national estimate of ambient contributions to surface and shallow ground water. It could also be used to provide point and non-point source aggregate concentrations within specific watersheds as a function of time (season) for total exposure assessment purposes.

The relative loads or fluxes of the oxygenates to surface and ground waters from point sources versus diffuse (nonpoint) sources must be more accurately determined. A possible approach to addressing this need might be the identification of a “source signature” for oxygenates that would permit reliable source identification, and perhaps even source apportionment, when used in conjunction with fate models. Although the identification of a source signature would be very useful, the feasibility of doing so is unclear, and attempts to provide similar signatures for other environmental contamination problems do not provide much cause for optimism. Consequently, this has to be rated as a lower priority than the development of the multimedia model described above.

## 3. TRANSPORT

### 3.1 Background

Oxygenates may enter both surface and ground water from diffuse and point sources (see Section 2, Source Characterization). In the case of scavenging from the atmosphere to precipitation, numerical modeling by Pankow et al. (1997) indicates that MTBE would transfer rapidly from the unsaturated zone into the saturated zone. However, no field observations of MTBE concentrations in ground water during and after precipitation or snow melt events are known to have been conducted.

The transport of oxygenates, particularly MTBE, through aquifers would be expected to occur at nearly the same velocity as the ground water. In a mixed composition contaminant source, such as is found in oxygenated fuels, each individual component will travel at a rate dependent on its water solubility and sorption tendency for soil. Oxygenates generally are more soluble in water and less sorbed to soils than any of the BTEX compounds. Given sufficient time and distance, each component of the mixture will separate within the plume according to basic chromatographic principles. Consequently, over time, MTBE and other oxygenates would be expected to be at the leading edge of the plume or, in the extreme case over a long period of time, could become completely separated from the rest of the plume if the original source of oxygenate were eliminated. If biodegradation of the oxygenate occurs (see Section 4, Transformation), it will interact with the transport process such that the front may appear to recede or be stabilized.

Generally, aquifer vulnerability to oxygenate contamination can be predicted using current wellhead protection models on a case-by-case basis. The required parameters for these models are hydrologic, geologic, and contaminant-specific. The required chemical data for modeling oxygenate transport are generally known, but again, transformation rates for the subsurface soil, vadose zone, and aquifers are required to run these models. The vulnerability of deep aquifers to oxygenate contamination is not well documented. In particular, the threat to deep aquifers due to abandoned wells and/or karst topography has not been assessed. Similarly, the threat to surface streams and lakes has not been assessed, even though suitable fate models for both exist. Again, adequate oxygenate loading models and fate parameters are needed to apply these models, particularly biodegradation rates, photolysis rates, and net air-water exchange rates.

## **3.2 Needs**

Given the progress made in the last several years on the modeling of the fate (transport and transformation) of organic compounds, particularly the BTEX compounds, in soils, ground water, and surface water, reasonable estimates of transport between and through environmental media can be made for oxygenates. For example, it is understood that MTBE would be expected to move through soil and ground water at a higher rate than BTEX compounds because it is more water soluble and less retarded by the solid matrix than the BTEX compounds. However, the impact that biodegradation will have on MTBE plume movement is less well understood. The greatest need, therefore, is to determine biodegradation rates for MTBE, other oxygenates, and their by-products under typical soil-groundwater transport conditions (as outlined in Section 4, Transformation). Field studies are needed to validate modeled rates of MTBE infiltration during precipitation events to determine the extent to which diffuse sources contribute to groundwater contamination, particularly shallow aquifers used for private wells. Three dimensional delineation of MTBE plume morphology in a variety of hydrological settings can be accomplished using push sampling techniques at multiple levels. Deep aquifer vulnerability should be examined by applying state-of-the-art fate models for scenarios that include karst-fractured flow effects and abandoned wells in areas that have high oxygenate use.

Field studies of the type the USGS Toxics Program (Baehr et al., 1997) is conducting are needed to quantify the combined impact of precipitation, land use, and storm water management practices on oxygenate loadings to surface and ground waters, and to develop and test multimedia exposure models. Stream and lake threat assessments should also be conducted to bound the potential threats from both diffuse and point sources of oxygenates and their degradation products.

# **4. TRANSFORMATION**

## **4.1 Background**

Contaminants may be transformed through a variety of chemical, physical, or biological processes. As a result, the mass, toxicity, mobility, volume, or concentration of parent contaminants in soil and water may be altered. The resulting products of these transformation

processes may in turn pose either a greater or lesser risk. For surface water, potential transformation processes are biodegradation, photolysis, and hydrolysis. In ground water, the potential transformation processes include biodegradation and hydrolysis. In surface water, photolysis is the most important transformation process for ether oxygenates, and biodegradation is the most important process for alcohols. Basic photolytic and hydrolytic processes are adequately understood.

Studies on the rates and pathways of environmental MTBE biodegradation are inconclusive, in part because they have been conducted under different conditions. For example, Sulflita and Mormile (1993) reported no biodegradation of MTBE in lab microcosms under a variety of aerobic and anaerobic conditions, using sediments from a petroleum-contaminated site. Salanitro et al. (1994), however, reported complete mineralization of MTBE to CO<sub>2</sub> in a mixed culture that was continuously sparged with oxygen. In another study (Petroleum Environmental Research Forum, 1993), MTBE was biodegraded when inoculated with a specific bacterial enrichment but not when inoculated with activated sludge. Limited biodegradation was observed in sediments under methanogenic conditions (Mormile et al., 1994) and in aerobic microcosms constructed with aquifer material obtained in the vicinity of the source area of a plume of dissolved BTEX and MTBE (Borden et al., 1997). Steffan et al. (1997) found that a number of propane-oxidizing bacteria were able to degrade high concentrations of MTBE, ETBE, and TAME. A series of degradation products were formed but did not prove to be effective growth substrates. Marked reduction in the concentrations of MTBE and benzene following termination of active remediation of fuel contamination was also observed in another plume at the same site (Cho et al., 1997).

The above studies do not constitute a comprehensive summary of efforts to evaluate the biodegradation of MTBE and other oxygenates, but they do illustrate the variety of results that have been observed. Most are laboratory studies, and the results are not necessarily representative of what might occur in the field. In addition, the observed rates of degradation vary widely, and this variability will impact the applicability of biodegradation as a remedial option.

Products of MTBE biodegradation include TBA (Mormile et al., 1994). However, comprehensive identification of biodegradation products and reaction pathways has not been undertaken.

## 4.2 Needs

Biodegradation rates and pathways for MTBE and other oxygenates need to be measured experimentally to understand and predict the fate of these compounds in the environment, and to design cost-effective removal and remediation technologies. The rates of biodegradation will be key in understanding the fate of oxygenates in the subsurface, in developing in situ and ex situ contaminant treatments, in implementing natural attenuation protocols, and in conducting aquifer vulnerability modeling. Identification of by-products and characterization of their environmental fate are needed to develop a complete picture of the effects of oxygenates on the environment and consequently the risks they may pose. Natural or intrinsic bioremediation is being widely accepted as either a primary or “polishing” process for groundwater remediation. Rapid transport, coupled with a slow rate of biodegradation, if confirmed, could compromise the validity of this remediation strategy as it relates to MTBE and possibly other oxygenates.

Additional field-scale and complementary laboratory microcosm studies are needed for sites with a variety of geochemical conditions. The geochemical conditions should include a range of redox and pH conditions and several dissolved electron receptors (e.g., oxygen, nitrate, sulfate) common in contaminated groundwater systems to determine the importance of aerobic and anaerobic reactions in MTBE degradation. The laboratory studies should also investigate the rates of biodegradation for high, moderate, and low concentrations of oxygenates, particularly as the concentration approaches the cleanup standard. Transformation products need to be identified and quantified so that specific biochemical pathways and degradation product yields under different geochemical conditions can be determined. Field studies need to be designed and conducted in tandem with microcosm studies for validation purposes.

# 5. OCCURRENCE

## 5.1 Background

MTBE was the second most frequently detected volatile organic compound (VOC) in shallow ground water from selected urban areas monitored under the National Water Quality Assessment (NAWQA) program of the USGS during 1993 and 1994 (Squillace et al., 1996). Of 210 sampled wells and springs, 56 (27%) contained MTBE at a minimum reporting level of

0.2 µg/L. (For comparison, 28% contained chloroform and 5% contained benzene.) Sixty wells and one spring contained MTBE and/or BTEX (benzene, toluene, ethylbenzene, xylene—a group of chemicals found in gasoline); of these 61 sites, 79% had MTBE alone, and 13% had both MTBE and BTEX. Of all the urban wells and springs sampled, 3% had MTBE concentrations exceeding 20 µg/L. In another study by the USGS (Delzer et al., 1996), MTBE was the seventh most frequently detected VOC in municipal storm water at a minimum reporting level of 0.2 µg/L.

The USGS NAWQA program is designed to assess the status and trends in the quality of ground and surface water resources of the nation. The USGS NAWQA program began sampling surface waters across the nation for MTBE, TAME, ETBE, and DIPE in 1997 and currently has collected fuel oxygenate data for approximately 2,000 wells across the United States, with additional wells being sampled continually at a rate of 1,500 to 2,000 wells every 3 years. Regional studies are ongoing for New England aquifers (Grady, 1997), aquifers and surface waters of Long Island, New York and in New Jersey (Stackelberg et al., 1997), and fractured bedrock aquifers in Pennsylvania (Lindsey et al., 1997). To further assess regional scale MTBE occurrence, the USGS and EPA entered into a cooperative agreement to conduct a pilot study in 12 Northeastern states where MTBE has been extensively used as a gasoline additive. The pilot project will describe the occurrence and distribution of MTBE and other VOC's in drinking water sources through a stratified statistical sampling of recent public water supply system data (both ground water and surface water) and ambient ground water data (Grady, 1997). The project will be managed under the general direction of the USGS National Synthesis Program.

A report by Buscheck et al. (1998) provides additional insight into the occurrence of MTBE in relation to UST sites. The authors evaluated groundwater plume monitoring data from more than 700 service station sites in different regions of the country. MTBE was detected at approximately 83% of the sites, with about 43% of all sites having MTBE concentrations greater than 1,000 µg/L and approximately 17% having detectable concentrations up to 35 µg/L. The highest frequencies of detection occurred at sites of currently operating stations (n = 466) in Texas and Maryland (96 and 98%), with northern and southern California intermediate (83 and 84%), and Florida the lowest (76%). Similar but slightly lower rates of occurrence were found at sites with nonoperating stations (n = 243). Concentrations greater than 1,000 µg/L were found at 55% of the operating sites and 22% of the nonoperating sites. The authors suggested that

differences in the incidence and levels of MTBE occurrence among the states included in the study may be due to various factors, including hydrogeologic differences and differing histories of MTBE usage and UST upgrade efforts. Although these data cannot be considered a representative sample, they reinforce concerns that oxygenate contamination of ground water may be more than a localized phenomenon.

Limited data collected by EPA regional offices for the “Water Quality” chapter in the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) indicated that 51 public water suppliers have detected MTBE (out of seven states that responded). Since February 1997, the California Department of Health Services has required public water suppliers to monitor their drinking water sources (i.e., ground water and surface water) for MTBE. To date, over 2,600 drinking water sources (24%) of a total of approximately 11,000 sources in California have been sampled for MTBE (California Department of Health Services, 1998). Of these, 13 sources (0.5%) had detectable levels of MTBE using the minimum analytical reporting limit of 5 µg/L (10 ground water and 3 surface water), including five sources with samples exceeding California’s drinking water interim action level of 35 µg/L. These data are based on a practical quantification limit (PQL) of 5 µg/L. If all detections are considered, including possible false positives below 5 µg/L, 34 sources (1.3%) had detectable levels of MTBE. None of the surface water samples exceeded 35 µg/L.

To require monitoring of drinking water for a contaminant such as MTBE or other oxygenates, EPA must first promulgate regulations requiring the collection of the data, with monitoring schedules based on the size of the public water system. As required by the Safe Drinking Water Act (SDWA), amended in 1996 (U.S. Code, 1996), EPA has published a Contaminant Candidate List (CCL) (Federal Register, 1998). The CCL is a list of currently unregulated contaminants that may be subject to more extensive evaluation for occurrence and/or health impacts. MTBE is included on the final CCL. The CCL will also be a source of chemicals to evaluate for possible inclusion in the Unregulated Contaminant Monitoring rule, which is required by the SDWA to be promulgated by August 1999. Contaminants included in the forthcoming rule will be subject to required monitoring by the states.

According to a draft background document on “Options for the National Drinking Water Contaminant Occurrence Data Base” (U.S. Environmental Protection Agency, 1997b), MTBE is proposed for inclusion. If EPA’s Office of Water ultimately decides to promulgate rulemaking

that requires monitoring of one or more oxygenates, the data would go into the national occurrence database, which would be based on the Safe Drinking Water Information System (SDWIS). Again, the required collection of data on MTBE or other oxygenates is contingent upon a decision by EPA's Office of Water to require such monitoring, which remains to be determined.

The Clean Water Act, Section 305(b) (U.S. Code, 1977) requires that states and other participating jurisdictions submit water quality assessment reports every two years to EPA. Based on these reports, EPA prepares the National Water Quality Inventory Report to Congress. However, a state may or may not provide data on specific unregulated contaminants such as MTBE in 305(b) reports, depending on the individual state's water quality priorities.

The ether oxygenates can be analyzed with several standard EPA methods. The most reliable methods use purge-and-trap capillary column gas chromatography/mass spectrometry (GC/MS) such as EPA Drinking Water Method 524.2, EPA Waste Water Method 624, or EPA Solid Waste (SW-846) Method 8260. The USGS GC/MS method SH2020 has also been determined to be reliable for ether oxygenates (Connor et al., 1998). These GC/MS methods provide positive identification of specific constituents and, as such, they overcome the problem of false identification of coeluting constituents. Standard EPA methods that use a GC/photoionization detector (PID) (i.e., Drinking Water Method 502.2, Waste Water Method 602, and SW-846 Method 8021) can also be useful, but because identification with these methods is based on the period of time that a chemical is expected to take to pass through the capillary column, false positives are possible with coeluting constituents. Depending on the purpose of the analysis (e.g., UST site assessment, drinking water supply monitoring), the problem of false identification can be minimized by first determining if MTBE or another ether oxygenate is present with a GC/MS method, than performing analyses on additional samples with a GC/PID method (Lawrence Livermore National Laboratory, personal communication).

GC/flame ionization detector (FID) methods can be useful for detection of the alcohols as well as the ether oxygenates. However, as with PID, FID is subject to misidentification of coeluting compounds and, since FID is sensitive to all organic compounds, detection of specific compounds can be more difficult than with other equipment. Despite these problems, a two-dimensional GC/FID method for water samples with high hydrocarbon content has been

developed using a modified ASTM method D4815 (Galperin, 1998). This method has been approved for use in California.

## 5.2 Needs

As stated in the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) and affirmed by the NAS/NRC Review Committee (National Research Council, 1996), oxygenates should be added to existing VOC analyte schedules and as routine target analytes for VOCs in drinking water, waste water, surface water, ground water, and remediation sites. This monitoring should also include the known transformation products of oxygenates (see Section 4, Transformation). Long-term monitoring is needed to support trend analyses of possible changes in water quality and the potential for population exposures. However, some discretion could be exercised with respect to including oxygenates that have not been used or are not expected to be used to any appreciable extent, if by their inclusion the cost of such monitoring would be significantly increased.

The Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997) recommends that a national database for monitoring data should be developed cooperatively among relevant governmental and private organizations, to be administered by a single federal agency. At present, existing “national” databases appear to be limited in their respective scopes. The EPA SDWIS contains drinking water data from public water supply distribution systems, whereas the USGS National Water Inventory System (NWIS) database contains ambient water quality data. Assuming that oxygenates are added to VOC analyte monitoring lists, an effort should be made after a reasonable period (e.g., 3 to 5 years from now) to analyze these or other databases for trends in the occurrence of oxygenates in water. These analyses should be linked to exposure assessment efforts (see Section 6, Exposure) and evaluated for guidance as to whether more intensive monitoring or other actions are warranted. To the extent possible, monitoring efforts and database designs should be undertaken in a manner to relate qualitatively and quantitatively to exposure assessments for human populations and aquatic biota.

The most pressing research need related to analytical methods is to develop an accurate, cost-effective method for detection of alcohol oxygenates. Although a direct aqueous injection GC/MS method (Church et al., 1997) exists for detection of TBA, it may be cost prohibitive for

widespread use. Similarly, detection of ethanol and methanol is very difficult with existing methods. In addition, development of low cost, simple field methods for detection of ether oxygenates would be useful. Although field portable GC/PID methods can likely be adapted for this purpose, supportive research would be helpful for facilitating their widespread use.

## 6. EXPOSURE

### 6.1 Background

Based on limited monitoring/occurrence data (see above), a potential for exposure of biota and human populations to oxygenates exists. The key question is the magnitude and distribution of exposures. Among many factors that can affect exposure to oxygenate-contaminated water, unpleasant odor and taste have been reported as particularly notable in the case of MTBE in drinking water (e.g., Angle, 1991). However, it cannot be assumed that the sensory properties of oxygenates would prevent human population exposures to such contaminants. Individuals vary greatly in sensory and subjective reactions, and indeed, anecdotal reports suggest that some individuals may have regularly consumed drinking water contaminated with MTBE at levels exceeding 100 µg/L. Also, young children in particular could be exposed via infant formula and beverages prepared with oxygenate-contaminated water. Even if all human exposures to oxygenates could be averted by water treatment processes, exposure of biota to contaminated surface or ground water could still occur.

Taste and odor detection thresholds for MTBE have been reported as ranging from 24 to 135 µg/L for taste and from 15 to 180 µg/L for odor (Dale et al., 1997; Shen et al., 1997; Young et al., 1996; Prah et al., 1994; Vetrano, 1993a,b; American Petroleum Institute, 1993). Limited testing suggests that taste and odor thresholds may be somewhat lower for ETBE and TAME than for MTBE (e.g., Shen et al., 1997; American Petroleum Institute, 1993; Vetrano, 1993a,b). All of the above studies were conducted with small numbers of subjects, which cannot be considered representative of populations.

It is important to note that detection and recognition thresholds for taste and odor sensations are distinct from their hedonic properties, which involve dimensions such as the (un)pleasantness and intensity of the sensory experience. In one study (Dale et al., 1997), four

panelists were asked to describe the taste and odor of MTBE in odor-free water at concentrations ranging from 2 µg/L to 190 µg/L. At concentrations of 2 to 5 µg/L, the consensus judgment of the panelists was that the taste of MTBE could be described as “sweet.” At concentrations of 21 to 190 µg/L, the characterization was either “solvent” or “sweet solvent.” Similar characteristics were attributed to the odor of MTBE at concentrations of 21 to 190 µg/L. The panelists were also asked to rate the intensity of the taste and odor, which they considered “objectionable” at a concentration of approximately 50 µg/L for taste and at approximately 90 to 100 µg/L for odor. Note that these tests were conducted with nonchlorinated, odor-free water at 25 °C. Chlorination would likely raise the thresholds for the taste and odor of MTBE in water, and higher temperatures (e.g., for showering) would likely lower these thresholds.

Hedonic responses, along with considerations of consumer cost, convenience, and other factors, may figure importantly in the levels of contamination that individuals or communities will reject or accept (and consequently be exposed to) in their drinking water. For example, cognitive factors, including attitudes that may be shaped by information provided through the social milieu, may significantly influence sensory perception (Dalton, 1996). Thus, populations as well as individuals may vary considerably in sensitivity to, and tolerance of, odors and tastes, such that a given concentration of contaminant might be quite acceptable to a large majority of persons in one group and strongly rejected by an equal proportion in another (cf. Anderson et al., 1995).

Microenvironmental measurements of VOCs such as benzene and trichloroethylene in relation to household water usage (e.g., Lindstrom et al., 1994; Wilkes et al., 1996; McKone and Knezovich, 1991) point to the importance of considering multi-media, multi-route personal exposures. “Drinking water” is used in many ways besides direct ingestion, including food preparation (especially mixed in beverages and infant formula), dish washing, laundering, and bathing. In particular, showering affords a significant exposure potential by the inhalation and dermal routes, with variables such as water flow rate and temperature possibly influencing exposure levels (Giardino and Andelman, 1996). Although the volatility and other properties of oxygenates may differ from VOCs investigated thus far, the importance of microenvironmental personal exposures in connection with contaminated household water usage would appear to apply to oxygenates as well.

Aquatic, terrestrial, and marine biota are subject to exposure to acute and/or chronic releases of fuels and fuel additives. However, very little information exists to characterize

exposure pathways or exposed ecological receptors in relation to oxygenates (Carlsen et al., 1997).

## 6.2 Needs

At present, very little empirical information is available either on the overall distribution of exposures to oxygenates in water for the U.S. population as a whole or on “high-end” exposure scenarios where oxygenate contamination is already known to occur. One step toward determining the prevalence and level of potential exposures to oxygenates would be to obtain monitoring data from public water suppliers (see Section 5, Occurrence). However, establishing large-scale monitoring programs is probably not the most efficient or cost-effective means for characterizing the potential for human population exposures to oxygenates. Rather, statistically representative sampling of public and private water supplies, including wells, may afford a more cost-effective approach. By coupling such data with qualitative and quantitative data on water usage and consumption patterns, it should be possible to model human exposures to specified oxygenates for risk assessment purposes (cf. Brown, 1997). The USGS NAWQA program may help address part of this need through a stratified statistical sampling of wells across the United States. The National Health and Nutrition Examination Survey (NHANES) program might also be used to collect data on population exposures to oxygenates and their metabolites, for example, by sampling blood and drinking water for MTBE and TBA levels. Although the focus of this document is water contamination, exposure to oxygenates must ultimately be considered in terms of all relevant pathways and routes, including inhalation, ingestion, and dermal contact.

With respect to locales where oxygenate contamination of the public water supply has already been documented, the focus should be on evaluating potential personal exposure scenarios involving all household uses of oxygenate-contaminated water (e.g., for drinking, infant formula, food preparation, cleaning, bathing). Several studies of multi-route VOC exposures through showering and other uses of tap water (e.g., Weisel and Jo, 1996) provide a substantial foundation for modeling as well as empirical studies of oxygenate exposure. As a first step, modeling of personal exposures, possibly using integrative approaches that incorporate macro- and micro-environmental pathways and even pharmacokinetic aspects (Georgopoulos et al., 1997; Piver et al., 1997; Rao and Ginsberg, 1997), should be undertaken, using sensitivity analyses to identify areas of needed additional data. Although a substantial database already exists for the

pharmacokinetics of MTBE by inhalation (e.g., Borghoff et al., 1996), additional work is needed to supplement the limited pharmacokinetic data for the oral and dermal routes. Biomarkers of exposure (e.g., metabolites such as TBA) might warrant investigation, if exposures prove to be of sufficient concern.

More extensive data on odor and taste thresholds and hedonic responses are needed to determine whether or how exposures may be affected by sensory variables. The issue of what contaminant levels may be acceptable to different consumer populations is not an exposure assessment issue per se, but more data on thresholds and hedonic reactions would provide a stronger basis for determining consumer acceptance levels.

## 7. AQUATIC TOXICITY

### 7.1 Background

The aquatic toxicity of oxygenates has been briefly summarized in the Interagency Assessment of Oxygenated Fuels (Interagency Oxygenated Fuels Assessment Steering Committee, 1997). Toxicity data (LC-50 or EC-50 values) exist for MTBE, ETBE, TAME, DIPE, EtOH, and TBA for selected aquatic species (e.g., *Daphnia magna*, *Pimephales promelas*, *Carassius auratus*). However, EPA has not established water quality criteria for oxygenates for the protection of freshwater or marine aquatic life. The American Petroleum Institute has recently completed a search and evaluation of the extant literature on the acute and chronic toxicity of oxygenates for aquatic organisms and has provided the results of that search to EPA. From the data gaps identified through that effort, testing to fill critical needs for MTBE is expected to be completed in 1998. The EPA Office of Water may then decide to prepare water quality criteria for MTBE.

### 7.2 Needs

Current actions should provide an appropriate basis for later determining whether additional effects testing or research is needed.

## 8. HEALTH EFFECTS

### 8.1 Background

Most of the testing and research on the toxicity of oxygenates has been concerned with the effects of *inhaled* MTBE in laboratory animals and human volunteers. Virtually no information exists on the effects of *ingested* oxygenates on humans, with the notable exception of the extensive database on the health effects of ingested ethanol. However, in the absence of any evidence indicating that human populations are exposed to ethanol-contaminated drinking water, the well characterized health effects of ingested ethanol need not be considered here.

Few studies have examined the toxicity of MTBE in laboratory animals via the oral route of exposure (e.g., Belpoggi et al., 1995; Robinson et al., 1990; IIT Research Institute, 1992; Bio-Research Laboratories Limited, 1990). None of these studies has used drinking water as a medium for administering MTBE to animals; rather, they typically deliver MTBE mixed in corn or olive oil in a bolus dose through a tube into the stomach, which does not correspond very well to the manner in which drinking water is typically consumed by people. Apart from such methodological problems, other questions have been raised (e.g., by the National Research Council, 1996) about the use of some of these studies for risk assessment purposes. Thus, considerable uncertainty currently hampers attempts to characterize the health risks related to MTBE in drinking water, as illustrated by the absence of any quantitative health risk estimation in a recent Drinking Water Advisory on MTBE (U.S. Environmental Protection Agency, 1997a).

Oral toxicity data for other ethers are even more limited in availability, although some work on inhaled vapors of ETBE and TAME is currently being conducted under provisions of a TSCA Enforceable Consent Agreement (Federal Register, 1995). Ingested TBA has been evaluated in rats and mice in a chronic bioassay by National Toxicology Program (Cirvello et al., 1995). Long-term exposure to TBA in drinking water produced various toxicologic and carcinogenic effects, including increased incidences of kidney and thyroid tumors.

### 8.2 Needs

Given the limitations of available information on the oral toxicity of MTBE and the much greater database on the inhalation toxicity of MTBE, the question arises as to whether more oral toxicity studies should be initiated, or should inhalation toxicity data be extrapolated to estimate

oral toxicity risk. A significant effort is already being devoted to developing a physiologically based pharmacokinetic (PBPK) model for MTBE in rodents to support human health risk assessment (Borghoff et al., 1996). Although the model appears to accurately predict blood levels of MTBE and metabolites such as TBA at low inhalation exposure levels of MTBE, it does not yet predict TBA levels accurately in target tissues in rodents. If the model is to provide a basis for extrapolating from inhalation effects to oral toxicity, it must be able to predict TBA levels in blood and possible target organs such as the kidney, liver, or testis. Moreover, it must be adequate for extrapolation from rodents to humans. A pharmacokinetic study of human volunteers exposed to MTBE by inhalation, oral, and dermal routes is planned by the EPA Office of Research and Development. Such efforts need to be pursued in the near term until an adequate PBPK model exists to accurately predict levels of MTBE and metabolites such as TBA and possibly formaldehyde (HCHO) in rodent and human target organs, particularly under low-level exposure conditions. Ultimately, the net health risks from multi-pathway exposures to MTBE (e.g., via refueling and motor vehicle use as well as drinking water) must be assessed.

The options of initiating further oral toxicity studies or of using PBPK modeling to extrapolate from inhalation effects to oral toxicity risk are not mutually exclusive. A study of subchronic oral exposure to MTBE would provide better data on the potential for toxic effects as well as help validate a PBPK model for cross-route extrapolation. If the PBPK modeling effort should turn out not to be able to support such an extrapolation with reasonable confidence, then a new chronic bioassay may be needed to reduce the uncertainties in assessing human health risks from chronic exposure to MTBE in drinking water.

Questions about the human relevance of carcinogenic effects observed in laboratory rodents exposed to high concentrations of MTBE by inhalation (Bird et al., 1997) and ingestion (Belpoggi et al., 1995) also need to be resolved if uncertainties in current assessments of human cancer risk are to be reduced. In view of the weight necessarily attached to the few cancer bioassays on MTBE, it would be desirable to reexamine and confirm the pathology data from all of these studies. Alternative assays for carcinogenicity, such as transgenic mice (Tennant et al., 1995) and Medaka fish (Boorman et al., 1997) assays, could offer relatively rapid approaches for collecting additional data that could contribute to a weight-of-evidence determination as well as potentially shed light on the modes of action. Although the latter approaches are unlikely to provide dose-response information that would enhance quantitative potency estimation, which is a

critical need, and interpretation of negative results from these assays could be problematic, nevertheless they could provide supporting or confirmative evidence of certain tumor types and thus assist in interpreting the relevance of inhalation effects for drinking water exposure.

The database for TBA may be adequate to characterize the oral toxicity of TBA. Given the unknown but conceivable potential for human exposure to TBA either as a metabolite, as an oxygenate itself, or as a natural biodegradation product of MTBE in ground water, an assessment of the carcinogenic and noncarcinogenic health risks of TBA should be undertaken.

The best strategy for the other ethers may be to obtain pharmacokinetic data (some of which work is already underway or anticipated for the inhalation route) and take such information into account in designing and conducting oral toxicity testing of these ethers. This strategy is predicated on low usage of ethers other than MTBE. If occurrence or exposure data become available and suggest otherwise, the need for more intensive investigation of the pharmacokinetics and health effects of other ethers may be elevated. As for degradation products of oxygenates (other than TBA), more information on the occurrence and concentrations of these chemicals is needed to guide decision-making about which chemicals to test.

## **9. RELEASE PREVENTION**

### **9.1 Background**

Although the contribution of point source releases to the problem of environmental contamination from fuel oxygenates cannot be quantitatively characterized at present, such releases are clearly a matter of risk management concern. The compatibility of fuel storage and distribution system components with the fuel they contain has always been an issue for system component manufacturers, petroleum refiners and distributors, and regulators. Federal regulations (§280.32, Code of Federal Regulations, 1990) require that UST system components be compatible with the constituents they contain. The changing composition of gasoline, primarily with the addition of ethers and alcohols, has raised the question of whether all existing systems are compatible with newer fuels and fuel additives.

Steel tanks and piping are not thought to be significantly corroded by oxygenates (Douthit and Davis, 1988; Geyer, 1995), but the effects of oxygenates on fiberglass reinforced plastic

(FRP) tanks and piping have been less clear. Although MTBE and other fuel ethers have been shown not to cause corrosion of FRP (Douthit et al., 1988; Drake et al., 1995), manufacturers such as Owens-Corning (Bartlow, 1995) have indicated that they do not extend their 30-year warranties to older (pre-1984) FRP tanks exposed to alcohols, depending on the type and concentration of the alcohol used. No known published research has examined older tanks exposed to up to 10% ethanol.

The possibility exists that some UST system components, such as FRP tanks and piping and flexible piping, might be permeable to MTBE and other oxygenates. Such permeability might account for cases of MTBE contamination at gasoline stations in which no leak could be detected and no other gasoline constituents were found. However, some doubt exists that the relatively large molecular weight of MTBE would allow it to pass through FRP (Curran, 1997). The only known study of FRP permeability to fuel oxygenates evaluated gasoline with 10 percent ethanol and found no liquid gasoline loss after 31 days (Smith Fiberglass Products Inc., 1996). No known work has been conducted on FRP permeability to any other oxygenate.

Elastomer seals, used for gaskets and o-rings throughout UST systems and petroleum pipelines, may have compatibility problems with oxygenated fuels. An American Petroleum Institute (1994) survey indicated that petroleum pipeline and terminal managers had noticed significant deterioration of many different types of elastomers associated with fuel oxygenates. The study, however, did not discuss the specific types of oxygenates that caused specific problems, nor did it discuss the concentrations of the oxygenates. Many of the problems listed were likely caused by “neat” (pure) solutions of the oxygenates, but the study raises the concern that more dilute solutions could cause problems as well.

Another study (Alexander et al., 1994) tested six elastomers in various concentrations of MTBE, ETBE, TAME, ethanol, and methanol. They found that although three of the seals were not able to withstand neat MTBE, all of the seals were acceptable for use in solutions of all five oxygenates when concentrations were less than 20% (immersed for 168 h at 23 °C). Hotaling (1995) tested 15 elastomers at 46 °C for 6 mo and found significant deterioration of three types of elastomers when exposed to concentrations of only 5% MTBE in gasoline. As a result, Hotaling found that these seals may be “... unsuitable for even low percentages of MTBE.” In actual use, however, EPA is not aware of any reports of UST system elastomers failing and causing a release because of exposure to gasoline containing oxygenates.

In addition to liquid-phase oxygenates, compatibility with vapor phase oxygenates should also be considered. Because the vapor pressure of MTBE is much higher than many other gasoline constituents, gasoline vapors should theoretically have much higher concentrations of MTBE than are found in the liquid phase. These vapors would occur in the headspace of tanks and vapor recovery systems. In addition, liquid-phase MTBE-enriched condensate could form inside these vapor recovery systems. Hotaling (1995) tested elastomers exposed to MTBE vapors and found significant deterioration to some elastomers throughout the concentration ranges tested (5 to 100%).

Dispenser sumps, used to catch small amounts of fuel below gasoline dispensers, are typically made of high density polyethylene. Although these sumps should be checked periodically to remove any fuel, it is possible that some measurable quantities of gasoline and oxygenates could be released via the sumps. Another potential concern is tank liners. These are plastic tanks within tanks, typically used inside steel tanks that may have started to corrode, and are used to avoid replacing the original tank. Certain liner materials may not be compatible with oxygenated fuels (Meli, 1996).

## **9.2 Needs**

The issue of materials compatibility with oxygenated fuels may prove to be quite manageable. However, a number of unanswered questions need to be resolved to ensure that releases do not and will not occur. It is important to characterize fully the effects of ethers and alcohols on elastomers, FRP, and other components of pipelines and tanks, particularly after several years of aging. The potential for leakage is unknown for older (pre-1984) FRP tanks that may be exposed to high (e.g., 10%) concentrations of ethanol. Also, the possible permeability of MTBE through FRP tanks and piping or flexible piping cannot be ruled out with existing data. Additional research is needed to resolve contradictory findings on the compatibility of elastomer seals with MTBE. Vapor recovery systems need to be examined more closely in terms of compatibility with concentrated MTBE vapor. Dispenser sumps need to be evaluated to determine if they are a potentially significant source of releases. Independent research is needed on the compatibility of currently marketed tank liners with ethanol.

Although newer technologies and regulations are intended to reduce the problem of leaking UST systems for conventional fuels, the different chemical properties of the various

oxygenated fuels raise questions not only about the compatibility of existing systems but also about leak detection methodologies. Even though the differences in the physicochemical properties of oxygenated and non-oxygenated fuels may be small, modest research efforts may be required to reevaluate and confirm the performance and accuracy of in-tank and external leak detection and monitoring technologies.

Based upon the results of the above studies, new and improved approaches and technologies could be developed to repair or replace problem areas and to prevent future problems through the use of more advanced materials and design concepts.

## **10. CONTAMINANT REMOVAL**

### **10.1 Background**

Various methods are available for removing contaminants from soils, ground water, waste water, and drinking water. Many of these techniques are potentially applicable to contamination from oxygenates. However, very limited data exist on the technical feasibility and costs of implementing them for oxygenate removal under field-scale operating conditions. The following background discussion is not meant to differentiate these processes in their applications, but rather to address their general efficiency for soils or waters contaminated with MTBE or other oxygenates. The discussion also notes those technologies that may be appropriate for in situ subsurface remediation, those that may be more applicable to above ground treatment of contaminated ground water, and those that may be more suitable for drinking water treatment at the wellhead or in a drinking water treatment plant.

Water treatment to remove MTBE and other oxygenates will frequently be conducted as part of an overall treatment process to remove other contaminants such as benzene. Consequently, it is worthwhile to ask if an ongoing treatment process will also be effective for oxygenate removal. However, since the oxygenates have different physical and chemical properties, a technology that is suitable for one oxygenate may not be suitable for another.

Subsurface treatment methods are often classified as those that transform, immobilize, or fix the contaminants in situ, and those that extract the contaminant from the subsurface for ex situ treatment on the surface. Both types are potentially applicable to MTBE and other oxygenates.

In situ biological treatment is known to be effective for the BTEX component of fuels, but its effectiveness for oxygenates is subject to debate. The feasibility of an in situ bioremediation process depends on many factors, including the biodegradation rate, the redox conditions, and the presence of other contaminants. Data are very limited on the field application of in situ bioremediation to oxygenates either as part of an active treatment project or for natural attenuation.

Soil vapor extraction (SVE) is commonly used to remove gasoline contaminants from the unsaturated zone at spill sites. Based on its high vapor pressure and low affinity for organic carbon in soil, MTBE would be expected to be readily removed from soil by vapor extraction. A computer model, VENT2D, has been used to simulate this process for a gasoline-MTBE mixture (Benson, 1994). In this simulation, MTBE showed the highest rate of mass loss of five gasoline components, as would be predicted based on their relative vapor pressures. Hence, MTBE and other ethers with high vapor pressures are not expected to be problematic for this technology. Grady and Johnson (1995) empirically demonstrated that SVE was successful in recovering MTBE, and as expected, the recovery of MTBE was greater than the recoveries for BTEX compounds.

Low-temperature thermal desorption (LTTD) is an ex situ soil treatment technology that uses temperatures below ignition levels to separate volatile contaminants from soil. Due to the high vapor pressure of MTBE, LTTD should be very effective in removing MTBE from soil. However, because MTBE separates from gasoline and dissolves quickly in water, both SVE and LTTD must be used soon after a release; otherwise most of the MTBE may have already moved from the soil into the ground water.

Air sparging involves the injection of air below the water table. The mechanisms for removal are stripping and potentially oxygen-enhanced biodegradation. Bass (1996) found that air sparging removed MTBE from ground water, with down-gradient wells showing 99% removal of MTBE. MTBE levels continued to decline for 13 mo after the air sparging unit was shut off, presumably due to aerobic degradation. Similar results were also reported by Cho et al. (1997).

Because MTBE does not adsorb well to soil and is highly soluble in water, “pump and treat” technology (i.e., pumping contaminated ground water and treating it above ground) may be effective in conjunction with certain above-ground biological or physical/chemical contaminant-removal processes for MTBE. Conditions such as the presence of complex

hydrogeology that create “dead” zones that are isolated from zones of high hydraulic conductivity will reduce the effectiveness of pump and treat for MTBE, despite its favorable chemical and physical characteristics.

Studies have indicated that MTBE biodegrades in ex situ biological treatment systems under aerobic and anaerobic conditions (see Section 4, Transformation). Once the conditions under which oxygenates biodegrade are fully defined, field work can be completed to determine the practicality of ex situ biological treatment for oxygenates removal.

Granular activated carbon (GAC) adsorption is a commonly used treatment process for organic contaminants. However, because of its limited adsorption capacity for MTBE, GAC is generally not cost effective for removing MTBE (Speth and Miltner, 1990). Therefore, it is not expected that adsorption would be generally used for removing MTBE on a large scale. This is especially true at high influent concentrations that would limit the time that a GAC column could be effective. For public water supplies, field studies have shown that carbon adsorption is not cost effective for MTBE removal unless the concentrations are very low (McKinnon and Dyksen, 1984). For example, even with an influent concentration of 30 µg/L, the carbon beds needed to be regenerated frequently. Other ether oxygenates have slightly lower solubilities than MTBE and thus would be more effectively adsorbed. However, alcohol oxygenates such as EtOH and TBA are infinitely soluble, and thus adsorption would be ineffective for these compounds. Carbon adsorption might be useful as a polishing step to air stripping.

Malley et al. (1993) have shown that MTBE adsorbs more strongly to synthetic adsorbents than to GAC. However, the capital cost of the synthetic adsorbents was much higher than that of GAC. This resulted in a conclusion that synthetic adsorbent removal of MTBE was not economically feasible. Synthetic adsorbents could be economically feasible for oxygenate removal if an inexpensive in situ regeneration process such as steam could be used (Malley et al., 1993).

For volatile organic compounds, air stripping is a cost effective alternative. However, the Henry’s constant for MTBE is low, indicating a relatively low efficiency for air stripping. Air stripping at a very high air-to-water ratio (e.g., 200:1) has been found effective in removing 93 to 99% of MTBE from ground water (McKinnon and Dyksen, 1984; American Petroleum Institute, 1990), but at air-to-water ratios of 44:1, 75:1, and 125:1 the percentage of MTBE removed was 44, 51, and 61%, respectively (McKinnon and Dyksen, 1984). By comparison, an effective air-to-water ratio for benzene is typically near 50:1. High air-to-water ratios can lead to severe operating

problems such as scaling and freezing during cold weather operations. McKinnon and Dyksen (1984) found that the cost of air stripping treatment was approximately 55% of that for carbon treatment. However, the off gas of the air stripping unit was not treated. Treating the off-gas stream would approximately double the cost of the air stripping system. Air stripping followed by GAC adsorption was found to be very effective for MTBE removal in this study, as also was found by Truong and Parmele (1992). Other oxygenates such as ETBE, TAME, and DIPE have higher Henry's constants than MTBE (from 3 to 20 times higher, roughly), which indicates that air stripping would be at least slightly more effective for them. For example, in the study by McKinnon and Dyksen (1984) the percentage removal of DIPE at an air-to-water ratio of 200:1 was greater than 99% (McKinnon and Dyksen, 1984). However, alcohol oxygenates have very low Henry's constants, indicating that air stripping would not be effective for these compounds.

Yeh (1992) found that hydrogen peroxide in the presence of iron (Fenton's reaction) degraded ETBE and MTBE. This was later confirmed under laboratory conditions by Chen et al. (1995) and other researchers. Therefore, the hydroxyl radicals produced by Fenton's reaction appear to be an effective treatment agent. Ozone/ultraviolet (UV), ozone/peroxide, and UV/peroxide also have potential as treatment technologies for oxygenate destruction. The American Petroleum Institute (1991) reported that advanced oxidation is more cost effective than other zero emission technologies such as steam stripping, ex situ biological oxidation, and air stripping with off-gas control. Malcolm Pirnie Incorporated (1997) also concluded that advanced oxidation is more cost-effective than carbon adsorption or air stripping with off-gas control. Malley et al. (1993) reported over 95% removal of MTBE using UV/peroxide. Oxidation byproducts included methanol, formaldehyde, and 1,1-dimethylethyl formate. Using UV/peroxide with a highly contaminated ground water produced less removal (up to 83%) presumably due to the effects of alkalinity scavenging of hydroxyl radicals and competition from other organics (Malley et al., 1993). The American Petroleum Institute (1997) reported up to 98% removal of MTBE in a UV/peroxide reactor under various conditions. DIPE had higher removal rates than MTBE, indicating that DIPE is more easily destroyed by hydroxyl radicals than MTBE. MTBE had reaction rate constants seven times lower than that for benzene, indicating that MTBE is only moderately reactive.

Because advanced oxidation systems increase the biodegradability of the organic matter in the water, biofiltration may be recommended following oxidation to control for biogrowth in

drinking-water distribution systems. The result could be an effective two-stage process: abiotic oxidation followed by aerobic biodegradation of the oxygenates.

## **10.2 Needs**

Numerous areas of contaminant-removal research need to be completed for MTBE and other oxygenates. Because remediation and drinking water sites often differ with regard to contaminant concentration, clean-up goals, secondary-effect issues such as biological regrowth and corrosion, and public acceptability, this section is separated into remediation and drinking-water subsections. For both subsections, comparative cost estimates for all technologies are needed.

The research needs for the removal of oxygenates from waste water are not discussed in this section. It is unknown as to the need for widespread treatment of waste waters for oxygenate removal. This is especially true when combined sewer and stormwater runoff issues are considered. Waste waters typically contain higher levels of background organics and inorganics that may interfere with the removal of oxygenates. Biological treatment (e.g., activated sludge, trickling filters) is commonly practiced for wastewater streams. Therefore, oxygenates may be removed from wastewater streams by biodegradation and stripping mechanisms within these technologies. Consequently, many of the research needs discussed below will be pertinent to the removal of oxygenates from waste water. This is especially true of biological degradation, which is extensively covered in Section 4 (Transformation).

### **10.2.1 Remediation Needs**

Remediation research is needed for both in situ remediation and ex situ cleanup of extracted ground water. This research should build on and expand earlier and ongoing work on remediation of ground water contaminated by other organic compounds. Research is likely to be most productive if it focuses initially on evaluating the applicability of known remediation technologies and adapting them to remediation of MTBE and other oxygenates. Cost as well as technical feasibility should be examined.

There is a pressing need for data about biodegradation (see Section 4, Transformation). Optimal conditions for biodegradation processes for in situ and ex situ contaminant removal need to be determined. This information is needed both to develop enhanced bioremediation

technologies and to better understand the applicability of natural attenuation and risk based corrective action at UST sites with oxygenate contamination. A particular focus should be on the introduction of oxygen and nutrients for in situ plume treatment and the potential for abiotic oxidation and aerobic biodegradation in porous-reactor barriers. Data are needed from field research and supporting laboratory studies under a variety of conditions, including different geochemical conditions, presence of other contaminants, and oxygenate concentrations. Information gathered from research regarding optimal biological conditions for oxygenate removal may lead to cost-effective remediation processes. Research on in situ abiotic oxidation is a lower priority.

Extraction processes, including pump and treat, SVE, LTDD, in-well stripping, dual-phase extraction, and air sparging need to be further evaluated. Specifically, the optimal operating conditions, effectiveness, and costs of these processes need to be investigated for MTBE and other oxygenates. Also, off-gas control for SVE, air sparging, in-well extraction, and LTDD need to be addressed when appropriate. Finally, the effect of temperature on Henry's Law constants for the entire class of oxygenates needs to be studied.

There is a strong need for research to develop and evaluate both biotic and abiotic surface treatment systems for extracted ground water. Air stripping is known to work, but many locations may require off-gas treatment. Research is needed to determine the effectiveness and cost of off-gas control. Promising research on bioreactors should be continued. For ex situ abiotic oxidation, Fenton's reagent, ozone/UV, ozone/peroxide, and UV/peroxide need to be further evaluated in terms of efficiency and cost under a variety of operating conditions. By-products of oxygenate degradation need to be identified under different conditions. By-product destruction may also need to be evaluated. These oxidative processes need to be optimized so that a site demonstration can be conducted to determine their cost effectiveness. GAC is not likely to be cost effective as an ex situ treatment process for MTBE in water, but it may have applicability to situations with low flow and low concentrations.

Sorbents such as vermiculite, straw, and peat have been proposed for oxygenate removal. Although their low cost may offset their low adsorption capacities, this is a low priority research area and should be limited to gathering and evaluating existing information at this time.

## 10.2.2 Drinking-Water Treatment Needs

Drinking-water treatment research needs to focus on low concentrations of contaminants typically found in source waters. Two technologies that should be investigated first include air stripping and hydroxyl-radical processes. For air-stripping, a matrix of the effectiveness and cost needs to be completed for various conditions (e.g., with and without off-gas control), which would allow more direct comparison to other treatment technologies. Also, configurations other than packed-tower aerators should be evaluated. Finally, the effect of temperature on Henry's Law constants for the entire class of oxygenates needs to be thoroughly studied so as to aid in the design and evaluation of heated air stripping and steam stripping systems.

As for abiotic oxidation processes, a hydroxyl radical treatment, viz. Fenton's reagent, has been shown to be effective for MTBE. Because of secondary effects, it is unlikely that Fenton's reagent would be used in a drinking water facility. However, other hydroxyl radical processes that utilities have experience with, such as ozone/peroxide, ozone/UV, and peroxide/UV, need to be more extensively evaluated. Evaluating UV lamp technologies should be a part of this work. Oxidation byproducts should be identified under different conditions. Byproduct destruction may also need to be evaluated. These oxidative processes need to be optimized so that a site demonstration can be conducted to determine their relative cost effectiveness.

Also, as previously mentioned, oxidation processes have been shown to increase the biodegradability of natural organics in water. Therefore, biofilters may be used in drinking water plants to control distribution-system regrowth. The removal of oxygenates and oxygenate degradates or byproducts in these biofilters should be studied. Limited data exist for biodegradation under drinking-water conditions, but the increase in biodegradability of natural organics due to hydroxyl-radical treatment potentially holds promise for the removal of oxygenates and their degradates as a secondary substrate, even at low concentrations. Any drinking water biodegradation work must concentrate on removing low levels of oxygenates.

Other biofiltration processes that utilize the addition of primary substrates should not be conducted under the auspices of drinking water treatment research. Primary substrates added to drinking water treatment streams are potentially problematic for several reasons: the primary substrate could contribute to deleterious human health effects; the primary substrate or its degradation byproducts might serve as disinfection byproduct precursor material; biogrowth might occur in the distribution system; and public dissatisfaction might result for these and other reasons.

Other drinking-water contaminant removal processes that need to be evaluated include GAC, carbonaceous adsorbents, and new bioreactor membrane technologies. For GAC, work needs to be completed in developing a matrix of the effectiveness and cost under various conditions. Because of its expected poor removal of oxygenates, specific research should be conducted with regard to using GAC as a polishing step for air stripping technologies, or as a biologically-active filter. Desorption from GAC also should be studied.

Synthetic carbonaceous adsorbents are very effective in removing many types of organic compounds from water. In general, steam is very effective for reversing adsorption processes for weakly adsorbing contaminants such as MTBE. Therefore, a study of an automated system that would adsorb oxygenates then desorb (regenerate) under steam conditions should be initiated.

An automated reverse osmosis system may be applicable for small utilities (under 500,000 gal/day). However, the potential for success for reverse osmosis is limited due to the low molecular weights (32 to 102 Daltons) of most oxygenates, and thus only a quick, low-cost evaluation of this process is warranted. Other membrane devices such as carbon-fiber bioreactor membranes may be more effective; however, preliminary information is needed before extensive research is conducted.

## 11. CONCLUSIONS

Certain priorities emerge from the foregoing discussion. Without attempting to place them in rank order, the following set of needed studies should be given priority consideration:

- Determination of the relative contributions of point and non-point sources of oxygenate fluxes to surface and ground waters
- Determination of oxygenate biodegradation rates and pathways under representative geochemical conditions, and identification of degradation by-products and their environmental fate
- Inclusion of oxygenate analytes and principal suspected transformation products wherever VOC monitoring of water is routinely performed
- Statistically representative sampling of public and private water supplies and modeling of multi-media, multi-pathway personal exposures for estimating population distributions of exposures; modeling and empirical studies of “high-end” microenvironmental exposure scenarios
- Completion of PBPK modeling and cancer mechanistic studies to enhance confidence in extrapolating from laboratory animal inhalation toxicity data as a basis for estimating oral toxicity risk of MTBE for humans; subchronic oral toxicity study of MTBE in drinking water
- More extensive evaluation of oxygenate effects on materials used in tanks and pipelines, especially after aging over a period of years
- Evaluation of the relative cost-effectiveness of candidate technologies for removing oxygenate contaminants from water under various conditions, with iterative efforts to optimize the most promising technologies, develop new innovative approaches, and evaluate the comparative cost effectiveness of available technologies
- Updating of risk characterizations as results of the above work become available

Efforts to address the issues identified in this document have been underway for some time, and new efforts are continually being initiated. Consequently, it is very difficult to describe the current state of the science in an accurate, up-to-date manner. Appendix 2 contains a listing of current projects related to oxygenates in water. The descriptions of projects are hardly adequate to convey the extent of work being undertaken, but the intent is to provide readers an impression of the scope of studies underway and information to assist readers if they wish to obtain further information about any particular project.

The purpose of conducting the work identified in this document is to provide a better basis for characterizing the potential health and environmental risks of oxygenates and for informing risk management and policy decision making. Risk assessment and risk management efforts directed at oxygenates in water have been occurring and will continue, regardless of whether adequate data exist to support these efforts. Without adequate scientific information and technical data, these efforts may be neither adequately protective of the environment and public health nor cost-effective.

## REFERENCES

- Alexander, J. E.; Ferber, E. P.; Stahl, W. M. (1994) Avoid leaks from reformulated fuels: choose an elastomeric sealing material according to the type and concentration of oxygenate (ether and/or alcohol) added to the fuel. *Fuel Reformulation* 4(Mar/Apr): 42-46.
- American Petroleum Institute. (1990) A compilation of field-collected cost and treatment effectiveness data for the removal of dissolved gasoline components from groundwater. Washington, DC: American Petroleum Institute; API publication no. 4525.
- American Petroleum Institute. (1991) Cost-effective, alternative treatment technologies for reducing the concentrations of methyl tertiary butyl ether and methanol in groundwater. Washington, DC: American Petroleum Institute; API publication no. 4497.
- American Petroleum Institute. (1993) Odor threshold studies performed with gasoline and gasoline combined with MTBE, ETBE and TAME. Washington, DC: American Petroleum Institute; API publication no. 4592.
- American Petroleum Institute. (1994) Effects of oxygenated fuels and reformulated diesel fuels on elastomers and polymers in pipeline/terminal components. Washington, DC: American Petroleum Institute; API publication 1132.
- American Petroleum Institute. (1997) Field evaluation of biological and nonbiological treatment technologies to remove MTBE/oxygenates from petroleum product terminal wastewaters. Washington, DC: American Petroleum Institute; API publication no. 4655.
- Anderson, H. A.; Hanrahan, L.; Goldring, J.; Delaney, B. (1995) An investigation of health concerns attributed to reformulated gasoline use in southeastern Wisconsin: phase 1, random digit dial telephone survey, final report. Madison, WI: Wisconsin Department of Health and Social Services, Division of Health, Bureau of Public Health; May 30.
- Angle, C. R. (1991) If the tap water smells foul, think MTBE [letter]. *JAMA J. Am. Med. Assoc.* 266: 2985-2986.
- Baehr, A. L.; Ayers, M. A. (1997) Occurrence and movement of contaminants through the urban hydrologic cycle—FY97 workplan update [for NAWQA Comprehensive Urban Study]. West Trenton, NJ: U.S. Geological Survey, Long Island-New Jersey National Water-Quality Assessment Program; February 1.
- Baehr, A. L.; Stackelberg, P. E.; Baker, R. J.; Kauffman, L. J.; Hopple, J. A.; Ayers, M. A. (1997) Design of a sampling network to determine the occurrence and movement of methyl tert-butyl ether and other organic compounds through the urban hydrologic cycle. In: American Chemical Society Division of Environmental Chemistry preprints of papers, 213th, San Francisco, CA: ACS, v. 37, p. 400-401
- Bartlow, D. (1995) [Letter to Owens-Corning tank customers clarifying the use of fiberglass underground storage tanks produced by Owens-Corning for the storage of ether and alcohol fuel blends]. Toledo, OH: Owens-Corning World Headquarters; April 14.
- Bass, D. H. (1996) Performance of air sparging systems: a review of case studies [unpublished presentation notes]. Norwood, MA: Groundwater Technology, Inc.
- Belpoggi, F.; Soffritti, M.; Maltoni, C. (1995) Methyl-tertiary-butyl ether (MTBE)—a gasoline additive—causes testicular and lymphohaematopoietic cancers in rats. *Toxicol. Ind. Health* 11: 119-149.
- Benson, D. (1994) VENT2D, Ver. 1.3. Reno, NV.

- Bio-Research Laboratories Limited. (1990) Mass balance of radioactivity and metabolism of methyl *tert*-butyl ether (MTBE) in male and female Fischer 344 rats after intravenous, oral and dermal administration of <sup>14</sup>C-MTBE. Senneville, Quebec, Canada: Bio-Research Laboratories Ltd.; report no. 38843.
- Bird, M. G.; Burleigh-Flayer, H. D.; Chun, J. S.; Douglas, J. F.; Kneiss, J. J.; Andrews, L. S. (1997) Oncogenicity studies of inhaled methyl tertiary-butyl ether (MTBE) in CD-1 mice and F-344 rats. *J. Appl. Toxicol.* 17(suppl. 1): S45-S55.
- Boorman, G. A.; Botts, S.; Bunton, T. E.; Fournie, J. W.; Harshbarger, J. C.; Hawkins, W. E.; Hinton, D. E.; Jokinen, M. P.; Okihira, M. S.; Wolfe, M. J. (1997) Diagnostic criteria for degenerative, inflammatory, proliferative nonneoplastic and neoplastic liver lesions in medaka (*Oryzias latipes*): consensus of a National Toxicology Program Pathology Working Group. *Toxicol. Pathol.* 25: 202-210.
- Borden, R. C.; Daniel, R. A.; LeBrun, L. E., IV; Davis, C. W. (1997) Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer. *Water Resour. Res.* 33: 1105-1115.
- Borghoff, S. J.; Murphy, J. E.; Medinsky, M. A. (1996) Development of a physiologically based pharmacokinetic model for methyl *tertiary*-butyl ether and *tertiary*-butanol in male Fischer-344 rats. *Fundam. Appl. Toxicol.* 30: 264-275.
- Brown, S. L. (1997) Atmospheric and potable water exposures to methyl *tert*-butyl ether (MTBE). *Regul. Toxicol. Pharmacol.* 25: 256-276.
- Buscheck, T. E.; Gallagher, D. J.; Kuehne, D. L.; Zuspan, C. R. (1998) Occurrence and behavior of MTBE in groundwater. Presented at: Underground storage tank conference: '98 & beyond; April; Los Angeles, CA. Sacramento, CA: State of California Water Resources Control Board.
- California Department of Health Services. (1998) Summary of sampling of public drinking water systems for methyl tertiary butyl ether (MTBE): covers data through February 20. Sacramento, CA: Prevention Services, Division of Drinking Water and Environmental Management; <http://www.dhs.cahwnet.gov/prevsrv/ddwem/MTBE.htm>.
- Carlsen, T.; Hall, L.; Rice, D. (1997) Ecological hazards of MTBE exposure: a research agenda. Springfield, VA: U.S. Department of Commerce, National Technical Information Service; report no. UCRL-ID-126290.
- Chen, C. T.; Tafuri, A. N.; Rahman, M.; Foerst, M. B.; Pftzing, E.; Taylor, M. (1995) Oxidation of methyl-*t*-butyl ether (MTBE) using Fenton's Reagent. Presented at: 88th annual meeting of the Air & Waste Management Association; June; San Antonio, TX. Pittsburgh, PA: Air & Waste Management Association; paper no. 95-WA91.03.
- Cho, J. S.; Wilson, J. T.; DiGiulio, D. C.; Vardy, J. A.; Choi, W. (1997) Implementation of natural attenuation at a JP-4 jet fuel release after active remediation. *Biodegradation* 8: 265-273.
- Church, C. D.; Isabelle, L. M.; Pankow, J. F.; Rose, D. L.; Tratnyek, P. G. (1997) Method for determination of methyl *tert*-butyl ether and its degradation products in water. *Environ. Sci. Technol.* 31: 3723-3726.
- Cirvello, J. D.; Radovsky, A.; Heath, J. E.; Farnell, D. R.; Lindamood, C., III. (1995) Toxicity and carcinogenicity of *t*-butyl alcohol in rats and mice following chronic exposure in drinking water. *Toxicol. Ind. Health* 11: 151-165.
- Code of Federal Regulations. (1990) Technical standards and corrective action requirements for owners and operators of underground storage tanks (UST); approval of state underground storage tank programs. C. F. R. 40: Parts 280 and 281.

- Connor, B. F.; Rose, D. L.; Noriega, M. C.; Murtagh, L. K.; Abney, S. R. (1998) Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory— determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits. Denver, CO: U.S. Geological Survey; open-file report 97-829.
- Curran, S. D. (1997) Permeability of synthetic membranes for the containment of petroleum products. Houston, TX: Fiberglass Tank & Pipe Institute; March.
- Dale, M. S.; Losee, R. F.; Crofts, E. W.; Davis, M. K. (1997) MTBE: occurrence and fate in source-water supplies. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. Natl. Meet. Am. Chem. Soc. Div. Environ. Chem. 37: 376-377.
- Dalton, P. (1996) Odor perception and beliefs about risk. *Chem. Senses* 21: 447-458.
- Delzer, G. C.; Zogorski, J. S.; Lopes, T. J.; Bosshart, R. L. (1996) Occurrence of the gasoline oxygenate MTBE and BTEX compounds in urban stormwater in the United States, 1991-95. Rapid City, SD: U.S. Geological Survey; water-resources investigations report 96-4145.
- Douthit, W. H.; Davis, B. C. (1988) 15% MTBE waiver request [submitted to Lee M. Thomas, U.S. Environmental Protection Agency, Washington, DC]. Sun Refining and Marketing Company. March.
- Douthit, W. H.; Davis, B. C.; De Lieu Steinke, E.; Doherty, H. M. (1988) Performance features of 15% MTBE/gasoline blends. Warrendale, PA: Society of Automotive Engineers, Inc.; report no. 881667.
- Drake, D. E.; Gregory, L. R.; Hotaling, A. C. (1995) Effect of MTBE and other oxygenates on FRP underground storage tanks - an interim report.
- Federal Register. (1995) Testing consent order for tertiary amyl methyl ether. *F. R.* (March 21) 54: 14910-14912.
- Federal Register. (1998) Announcement of the drinking water contaminant candidate list. *F. R.* (March 2) 63: 10,273-10,287.
- Galperin, Y. (1998) Gasoline oxygenate analysis in environmental samples by two-dimensional gas chromatography. Presented at: West coast conference on contaminated soil and groundwater; March.
- Garrett, P. (1987) Oxygenates as ground water contaminants. Presented at: 1987 conference on alcohols and octane; April; San Antonio, TX.
- Georgopoulos, P. G.; Walia, A.; Roy, A.; Lioy, P. J. (1997) Integrated exposure and dose modeling and analysis system. 1. Formulation and testing of microenvironmental and pharmacokinetic compounds. *Environ. Sci. Technol.* 31: 17-27.
- Geraghty & Miller, Incorporated. (1996) MTBE contamination forces well closures. *Groundwater Newsl.* 25(16): 1.
- Geyer, W. B. (1995) Compatibility of steel with oxygenated fuels. Presented at: API materials compatibility roundtable: an industry discussion; September; Cincinnati, OH.
- Giardino, N. J.; Andelman, J. B. (1996) Characterization of the emissions of trichloroethylene, chloroform, and 1,2-dibromo-3-chloropropane in a full-size, experimental shower. *J. Exposure Anal. Environ. Epidemiol.* 6: 413-423.
- Grady, S. J. (1997) Distribution of MTBE in ground water in New England by aquifer type and land use. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. Natl. Meet. Am. Chem. Soc. Div. Environ. Chem. 37: 392-394.

- Grady, D.; Johnson, R. L. (1995) Vapor extraction of a contaminated fractured clay. In: Petroleum hydrocarbons and organic chemicals in ground water: prevention, detection and remediation, proceedings of a conference. Dublin, OH: National Ground Water Association; pp. 593-604.
- Health Effects Institute. (1996) The potential health effects of oxygenates added to gasoline: a review of the current literature, a special report of the Institute's Oxygenates Evaluation Committee. Cambridge, MA: Health Effects Institute, Oxygenates Evaluation Committee.
- Hoff, J. T.; Gregor, D.; MacKay, D.; Wania, F.; Jia, S. Q. (1998) Measurement of the specific surface area of snow with the nitrogen adsorption technique. *Environ. Sci. Technol.* 32: 58-62.
- Hotaling, A. C. (1995) Evaluating nonmetallic materials' compatibility with MTBE and MTBE + gasoline service. In: American energy week '95 - pipelines, terminals & storage II: reformulated fuels conference proceedings. AST: special problems I; pp. 118-126.
- IIT Research Institute. (1992) Twenty-eight day oral (gavage) toxicity study of methyl *tert*-butyl ether (MTBE) in rats [final report]. Chicago, IL: IIT Research Institute; project no. L08100SN1602.
- Interagency Oxygenated Fuels Assessment Steering Committee. (1996) Interagency assessment of potential health risks associated with oxygenated gasoline. Washington, DC: National Science and Technology Council and Office of Science and Technology Policy.
- Interagency Oxygenated Fuels Assessment Steering Committee. (1997) Interagency assessment of oxygenated fuels. Washington, DC: National Science and Technology Council, Committee on Environment and Natural Resources and Office of Science and Technology Policy.
- Kneiss, J. (1998) Personal communication. Arlington, VA: Oxygenated Fuels Association.
- Lindsey, B. D.; Breen, K. J.; Daly, M. H. (1997) MTBE in water from fractured-bedrock aquifers, southcentral Pennsylvania. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. *Natl. Meet. Am. Chem. Soc. Div. Environ. Chem.* 37: 399-400.
- Lindstrom, A. B.; Highsmith, V. R.; Buckley, T. J.; Pate, W. J.; Michael, L. C. (1994) Gasoline-contaminated ground water as a source of residential benzene exposure: a case study. *J. Exposure Anal. Environ. Epidemiol.* 4: 183-195.
- Malcolm Pirnie Incorporated. (1997) Estimates of annual costs to remove MTBE from water for potable uses. Arlington, VA: Oxygenated Fuels Association, Inc.; technical memorandum no. 3195-001.
- Malley, J. P.; Locandro, R. R.; Wagler, J. L. (1993) Innovative point-of-entry (POE) treatment for petroleum contaminated water supply wells. Final report. Durham, NH: U.S. Geological Survey, New Hampshire Water Resources Research Center.
- McKinnon, R. J.; Dyksen, J. E. (1984) Removing organics from groundwater through aeration plus GAC. *J. Am. Water Works Assoc.* 76: 42- 47.
- McKone, T. E.; Knezovich, J. P. (1991) The transfer of trichloroethylene (TCE) from a shower to indoor air: experimental measurements and their implications. *J. Air Waste Manage. Assoc.* 41: 832-837.
- Meli, P. I., Jr. (1996) [Letter to Ms. Sonya Harrigfeld concerning Bridgeport Chemical Group's underground storage tank lining product]. Pompano Beach, FL: Industrial Environmental Coatings Corporation; August, 14.
- Mormile, M. R.; Liu, S.; Suflita, J. M. (1994) Anaerobic biodegradation of gasoline oxygenates: extrapolation of information to multiple sites and redox conditions. *Environ. Sci. Technol.* 28: 1727-1732.

- National Research Council; Committee on Toxicological and Performance Aspects of Oxygenated and Reformulated Motor Vehicle Fuels. (1996) Toxicological and performance aspects of oxygenated motor vehicle fuels. Washington, DC: National Academy Press.
- Pankow, J. F.; Thomson, N. R.; Johnson, R. L.; Baehr, A. L.; Zogorski, J. S. (1997) The urban atmosphere as a non-point source for the transport of MTBE and other volatile organic compounds (VOCs) to shallow groundwater. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. Natl. Meet. Am. Chem. Soc. Div. Environ. Chem. 37: 385-387.
- Petroleum Environmental Research Forum. (1993) Aerobic biodegradation of MTBE - basic fate of biokinetics evaluation, final report of PERF project 90-10, June, 1993.
- Piver, W. T.; Jacobs, T. L.; Medina, M. A., Jr. (1997) Evaluation of health risks for contaminated aquifers. Environ. Health Perspect. 105(suppl. 1): 127-143.
- Prah, J. D.; Goldstein, G. M.; Devlin, R.; Otto, D.; Ashley, D.; House, D.; Cohen, K. L.; Gerrity, T. (1994) Sensory, symptomatic, inflammatory, and ocular responses to and the metabolism of methyl tertiary butyl ether in a controlled human exposure experiment. Inhalation Toxicol. 6: 521-538.
- Rao, H. V.; Ginsberg, G. L. (1997) A physiologically-based pharmacokinetic model assessment of methyl *t*-butyl ether in groundwater for a bathing and showering determination. Risk Anal. 17: 583-598.
- Reuter, J. (1997) Grant proposal to the Office of Ground Water and Drinking Water, U.S. Environmental Protection Agency, Washington, DC. Davis, CA: Tahoe Research Group, University of California.
- Robinson, M.; Bruner, R. H.; Olson, G. R. (1990) Fourteen- and ninety-day oral toxicity studies of methyl tertiary-butyl ether in Sprague-Dawley rats. J. Am. Coll. Toxicol. 9: 525-540.
- Salanitro, J. P.; Diaz, L. A.; Williams, M. P.; Wisniewski, H. L. (1994) Isolation of a bacterial culture that degrades methyl *t*-butyl ether. Appl. Environ. Microbiol. 60: 2593-2596.
- Salanitro, J. P.; Diaz, L. A.; Williams, M. P.; Wisniewski, H. L. (1995) Erratum: Isolation of a bacterial culture that degrades methyl-*t*-butyl ether. Appl. Environ. Microbiol. 61: 406.
- Shen, Y. F.; Yoo, L. J.; Fitzsimmons, S. R.; Yamamoto, M. K. (1997) Threshold odor concentrations of MTBE and other fuel oxygenates. In: Preprints of papers presented at the 213th American Chemical Society national meeting; April; San Francisco, CA; pp. 407-409. (ACS Division of Environmental Chemistry: v. 37)
- Smith Fiberglass Products, Inc. (1996) Just the facts [permeability testing of piping systems manufactured by Smith Fiberglass Products]. Little Rock, AR: Smith Fiberglass Products, Inc.
- Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E.; McIver, C. D.; Bufalini, J. J. (1991) The photooxidation of methyl *tertiary* butyl ether. Int. J. Chem. Kinet. 23: 907-924.
- Speth, T. F.; Miltner, R. J. (1990) Technical note: adsorption capacity of GAC for synthetic organics. J. Am. Water Works Assoc. 82: 72-75.
- Squillace, P. J.; Zogorski, J. S.; Wilber, W. G.; Price, C. V. (1996) Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-1994. Environ. Sci. Technol. 30: 1721-1730.
- Squillace, P. J.; Zogorski, J. S.; Wilber, W. G.; Price, C. V. (1997) Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993-94. In: Chilton, J.; et al. Proceedings of the congress on groundwater in the urban environment; September; Balkema, Netherlands; pp. 537-542.

- Stackelberg, P. E.; O'Brien, A. K.; Terracciano, S. A. (1997) Occurrence of MTBE in surface and ground water, Long Island, New York, and New Jersey. In: Preprints of papers presented at the 213th ACS national meeting; April; San Francisco, CA. Natl. Meet. Am. Chem. Soc. Div. Environ. Chem. 37: 394-397.
- Steffan, R. J.; McClay, K.; Vainberg, S.; Condee, C. W.; Zhang, D. (1997) Biodegradation of the gasoline oxygenates methyl *tert*-butyl ether, ethyl *tert*-butyl ether, and *tert*-amyl methyl ether by propane oxidizing bacteria. Appl. Environ. Microbiol. 63: 4216-4222.
- Suflita, J. M.; Mormile, M. R. (1993) Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface. Environ. Sci. Technol. 27: 976-978.
- Tennant, R. W.; French, J. E.; Spalding, J. W. (1995) Identifying chemical carcinogens and assessing potential risk in short-term bioassays using transgenic mouse models. Environ. Health Perspect. 103: 942-950.
- Truong, K. N.; Parmele, C. S. (1992) Cost-effective alternative treatment technologies for reducing the concentrations of methyl tertiary butyl ether and methanol in groundwater. In: Calabrese, E. J.; Kostecki, P. T., eds. Hydrocarbon contaminated soils and groundwater: v. 2. Boca Raton, FL: Lewis Publishers; pp. 461-486.
- U. S. Code. (1977) Clean Water Act. U. S. C. 33: § 305(b).
- U.S. Code. (1990) Clean Air Act, §211, regulation of fuels: (k) reformulated gasoline for conventional vehicles; (m) oxygenated fuels. U. S. C. 42: §7545.
- U.S. Code. (1996) Safe Drinking Water Act, as amended by PL 104-208, September 30. U. S. C. 42: §300f et seq.
- U.S. Department of Energy. (1995a) Imports of crude oil and petroleum products by PAD district, 1995 [data from form EIA-841, monthly imports report]. In: Petroleum supply annual 1995: volume 1. Washington, DC: Energy Information Administration, Office of Oil & Gas; p. 55; report no. DOE/EIA-0340(95).
- U.S. Department of Energy. (1995b) Monthly oxygenate telephone report: form EIA-819M. In: Petroleum supply monthly: December. Washington, DC: Energy Information Administration, Office of Oil & Gas; p. 135; report no. DOE/EIA-0109(95/12).
- U.S. Environmental Protection Agency. (1992a) Alternative fuels research strategy. Research Triangle Park, NC: Environmental Criteria and Assessment Office; report no. EPA/600/AP-92/002.
- U.S. Environmental Protection Agency. (1992b) Measurement of purgeable organic compounds in water by capillary-column gas chromatography/mass spectrometry, method 524.2, revision 4.0. Cincinnati, OH: Environmental Monitoring Systems Laboratory; August.
- U.S. Environmental Protection Agency. (1993) Assessment of potential risks of gasoline oxygenated with methyl tertiary butyl ether (MTBE). Washington, DC: Office of Research and Development; November; report no. EPA/600/R-93/206.
- U.S. Environmental Protection Agency. (1994) Health risk perspectives on fuel oxygenates. Washington, DC: Office of Research and Development; report no. EPA 600/R-94/217.
- U.S. Environmental Protection Agency. (1996) Oxyfuels information needs. Research Triangle Park, NC: National Center for Environmental Assessment; report no. EPA/600/R-96/069. Available from: NTIS, Springfield, VA; PB96-190665REB.

- U.S. Environmental Protection Agency. (1997a) Drinking water advisory: consumer acceptability advice and health effects analysis on methyl tertiary-butyl ether (MTBE). Washington, DC: Office of Water; report no. EPA-822-F-97-008.
- U.S. Environmental Protection Agency. (1997b) Options for the National Drinking Water Contaminant Occurrence Data Base: background document (working draft) for the National Contaminant Occurrence Data Base stakeholders meeting May 21-22, 1997, Washington, D.C. Washington, DC: U.S. Environmental Protection Agency, Office of Water; pp. 10-14; report no. EPA 815-D-97-001.
- Vetrano, K. (1993a) Odor and taste threshold studies performed with tertiary-amyl methyl ether (TAME). Washington, DC: American Petroleum Institute; API publication no. 4591.
- Vetrano, K. M. (1993b) Final report to ARCO Chemical Company on the odor and taste threshold studies performed with methyl tertiary-butyl ether (MTBE) and ethyl tertiary-butyl ether (ETBE). Windsor, CT: TRC Environmental Corporation; project no. 13442-M31.
- Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. (1988) Gas-phase reactions of hydroxyl radicals with the fuel additives methyl *tert*-butyl ether and *tert*-butyl alcohol over the temperature range 240-440 K. Environ. Sci. Technol. 22: 842-844.
- Weisel, C. P.; Jo, W.-K. (1996) Ingestion, inhalation, and dermal exposures to chloroform and trichloroethene from tap water. Environ. Health Perspect. 104: 48-51.
- Wilkes, C. R.; Small, M. J.; Davidson, C. I.; Andelman, J. B. (1996) Modeling the effects of water usage and co-behavior on inhalation exposures to contaminants volatilized from household water. J. Exposure Anal. Environ. Epidemiol. 6: 393-412.
- Wyborny, L. A., II. (1997) Oxy-water res strategy question -reply [email memorandum to J. Michael Davis, U.S. EPA, RTP, NC]. Ann Arbor, MI: U.S. Environmental Protection Agency, Office of Mobile Sources; August 18.
- Yeh, K.-J. (1992) Degradation of gasoline oxygenates in the subsurface. Blacksburg, VA: Virginia Polytechnic Institute.
- Young, W. F.; Horth, H.; Crane, R.; Ogden, T.; Arnott, M. (1996) Taste and odour threshold concentrations of potential potable water contaminants. Water Res. 30: 331-340.

# APPENDIX 1

## CHEMICAL PROPERTIES OF SELECTED OXYGENATES

Chemical Name	Methyl Tertiary-Butyl Ether	Ethyl Tertiary-Butyl Ether	Tertiary-Amyl Methyl Ether	Diisopropyl Ether
CAS Registry No.	1634-04-4	637-92-3	994-05-8	108-20-3
Synonyms	MTBE; 2-methyl, 2-methoxy propane; tert-butyl methyl ether; methyl tert butyl ether; methyl-tert-butyl ether	ETBE; tert-butyl ethyl ether; propane, 2-ethoxy-2methyl; 1, 1-dimethyl ethyl ether	TAME; 2-methoxy-2 methylbutane; methyl tert-pentyl ether; 1,1-dimethylpropyl methyl ether; methyl tert-amyl ether	DIPE; 2'2-oxybispropane; 2-isopropoxypropane
Molecular Weight (g/mol)	88.15	102.18	102.18	102.18
Molecular Formula	C <sub>5</sub> H <sub>12</sub> O	C <sub>6</sub> H <sub>14</sub> O	C <sub>6</sub> H <sub>14</sub> O	C <sub>6</sub> H <sub>14</sub> O
Structural Formula	CH <sub>3</sub> OC(CH <sub>3</sub> ) <sub>3</sub>	(CH <sub>3</sub> ) <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHOCH(CH <sub>3</sub> ) <sub>2</sub>
Boiling Point (at 760 mm Hg)	55.2 °C	72.2 °C	86.3 °C	68.2 °C
Vapor Pressure (mm Hg at 20 °C)	240	130	75	159
Vapor Density (air = 1)	3.1	3.6	3.6	3.6
Density (g/ml at 20 °C)	0.74	0.74	0.77	0.73
Solubility (g/100 g water)	4.8	1.2	1.2	0.2
Henry's Law Constant				
(Atm-m <sup>3</sup> )/ (g-mole)	5.28E-4 to 3E-3	2.64E-3	1.95E-3	4.77E-3
Dimensionless	2.2E-2 to 1.2E-1	0.11	0.081	0.199
Log K <sub>oc</sub>	0.55 to 0.91	NA	NA	1.13
Log K <sub>ow</sub>	0.94 to 1.30	NA	NA	1.52

**CHEMICAL PROPERTIES OF SELECTED OXYGENATES (cont d)**

Chemical Name	Tertiary-Amyl Ethyl Ether	Dimethyl Ether	Tertiary-Butanol	Ethanol
CAS Registry No.	919-94-8	115-10-6	75-65-0	64-17-5
Synonyms	TAAE; ethyl tert-amyl ether; butane, 2-ethoxy-2-methyl	DME; methane, oxybis	TBA; tertiary butyl alcohol; 2-propanol, 2-methyl	EtOH; ethyl alcohol
Molecular Weight (g/mol)	116.20	46.07	74.12	46.07
Molecular Formula	C <sub>7</sub> H <sub>16</sub> O	C <sub>2</sub> H <sub>6</sub> O	C <sub>4</sub> H <sub>10</sub> O	C <sub>2</sub> H <sub>6</sub> O
Structural Formula	CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> OCH <sub>3</sub>	(CH <sub>3</sub> ) <sub>3</sub> COH	CH <sub>3</sub> CH <sub>2</sub> OH
Boiling Point (at 760 mm Hg)	102 °C	-24.8 °C	82.4 °C	78.5 °C
Vapor Pressure (mm Hg at 20 °C)	NA	758 to 5086 <sup>a</sup>	41	44
Vapor Density (air = 1)	4.0	1.6	2.6	1.6
Density (g/mL at 20 °C)	0.75	0.66	0.79	0.79
Solubility (g/100 g water)	NA	4.7 to 35.3	miscible	miscible
Henry's Law Constant				
(Atm·m <sup>3</sup> )/ (g·mole)	NA	4.89E-4 to 9.97E-4	1.21E-5	6.91E-6
Dimensionless	NA	2.03E-2 to 4.15E-2	5.03E-4	2.83E-4
Log K <sub>oc</sub>	NA	-0.29	1.57	-0.14
Log K <sub>ow</sub>	NA	0.10	0.35	-0.32

<sup>a</sup>At 25 °C

## APPENDIX 2

### CURRENT PROJECTS RELATED TO OXYGENATES IN WATER

Format:

Organization(s)  
Project title  
Contact person(s)  
Purpose  
Status  
Relevant topic area(s)

Alpine Environmental

MTBE Remediation: An Evaluation of Technologies, Field Experience, and Case Studies.

James Davidson, Alpine Environmental

Review and analysis of remediation technologies applicable for MTBE; discusses both theory and actual case studies.

Draft currently under peer review

Contaminant Removal; Assessment

American Petroleum Institute (MTBE Water Quality Criteria Workgroup) / EPA-OW

Eco/aquatic Biota Toxicity Literature Search

Gene Mancini, ARCO / Frank Gostomski, EPA-OW

After literature search to determine gaps in aquatic toxicity database, testing to develop data set to enable EPA to determine acute and chronic water quality criteria for MTBE in both fresh water and marine environs.

Report due in late 1998 or early 1999

Aquatic Toxicity

American Water Works Association Research Foundation

Sampling of Public Drinking Water Supplies

Kenan Ozekin, AWWARF

*RFP*: nation-wide sampling of drinking water to characterize MTBE contamination.

Funding being considered in spring, 1998; start work in late 1998; completion in 1999

Exposure; Occurrence

Assoc. Calif. Water Agencies / WSPA / OFA / CalEPA / EPA

MTBE Treatability Research Partnership

Krista Clark, ACWA / Dave Smith, ARCO

Joint research program to evaluate existing and emerging treatment technologies to remove MTBE from public drinking water supplies.

Proposal requires legal closure; report expected by mid-1999

Contaminant Removal

Billings and Associates, Inc.

Biosparging: "Firehouse site" (Shasta Co., CA)

Jeff Billings, BAI

Microorganisms from LUST sites found capable of degrading MTBE to non-detectable levels (starting at up to 1000 ppb); longer time required to achieve "standards" if starting at 5K-10K ppb, and may only reduce to 75-80% of original concentration.

Status?

Contaminant Removal; Transport & Transformation

Calif. Regional Water Quality Control Board - Los Angeles Region

MTBE Soil Remedial Concentration Based on Monte Carlo Simulation

Yue Rong, California Regional Water Quality Control Board - Los Angeles Region

Transport models and Monte Carlo simulation used to determine MTBE soil remedial concentration such that residual soil concentration will not result in groundwater concentration exceeding 35  $\mu\text{g}/\text{l}$  (CA advisory limit for MTBE in drinking water).

Paper presented at West Coast Conference on Contaminated Soil and Groundwater, March 9-12, 1998

Transport & Transformation; Contaminant Removal

Environmental and Occupational Health Sciences Inst. / ARCO Chem. / State of NJ

Inhalation Chamber Study of MTBE in Humans

Paul Lioy / Nancy Fiedler, EOHSI

Inhalation exposure to MTBE in gasoline evaluated in controls and in subjects self-described as sensitive to MTBE; although only inhalation route used, results might be relevant to other routes.

Ongoing; final report in fall, 1998

Health Effects

EPA-ORD

Natural Attenuation of MTBE in Ground Water and Soils

Fran Kremer and Steve Schmelling, EPA-ORD-NRMRL

Field and laboratory studies on UST sites impacted with MTBE; preparation of technical resource documents on natural biodegradation of MTBE and associated HCs in ground water and soils, and the potential for enhanced biodegradation.

Ongoing

Transport & Transformation; Contaminant Removal

EPA-ORD

Intrinsic Biodegradation of MTBE

John Wilson, EPA-ORD

EPA-ORD-NRMRL-Ada field and lab study evaluating the role of intrinsic biodegradation of MTBE in a fuel plume at Elizabeth City, NC; work initiated Fall 96.

Ongoing; report due late 1998

Transport & Transformation

EPA-ORD

Human Pharmacokinetics of MTBE

Jim Prah, EPA-ORD-NHEERL

Pharmacokinetics study of human volunteers given multiple acute exposures to MTBE by inhalation, oral, and dermal routes.

Work scheduled to start and finish in 1998; report due in 1999

Health Effects

EPA-ORD

Simulation of Multicomponent Gasoline Dissolution

Jim Weaver, EPA-ORD-NERL-ERD

Aquifer transport, leaching, and chemical property estimation models used to study multicomponent dissolution from MTBE- and non MTBE-gasolines, the effects of MTBE on dissolution of BTEX, and the minimum number of components required to simulate dissolution of a given gasoline component.

Currently incorporating any field data; paper due in August, 1998

Transport & Transformation

EPA-ORD / IT Corp.

Technologies for Remediating Petroleum-contaminated Soil.

Anthony Tafuri, Chien Chen, EPA-ORD-NRML-Edison

Studies (bench and pilot field) to investigate use of hydrogen peroxide in combination with ferrous iron (Fenton's Reagent) to oxidize MTBE in both soil and water; general objective is to identify any intermediate products that may develop in the treatment process and identify operational parameters ("Chemical Oxidation Treatment of Petroleum Contaminated Soil Using Fenton's Reagent," Journal of Environmental Science and Health, in press).

Estimated completion date September, 1998

Contaminant Removal

EPA-ORD / NY State DEC

Modeling Plume: East Patchogue and Uniondale

Jim Weaver, EPA-ORD-NERL / Joseph Haas, NY DEC

EPA-ORD-NERL-Athens 3-D monitoring and modeling of MTBE, BTEX in contaminant plume from LUST site on Long Island, NY; demonstration site for EPA Hydrocarbon Spill Screening Model (HSSM).

Data collected 1994 - 1996; case study paper available; MTBE transport model paper due July, 1998; BTEX model paper in December, 1998

Transport & Transformation

EPA-Region 9

Compiling LUST Monitoring Well Data: California

Cheryl Henley, Bill Robberson, EPA-Region 9

Compiling and plotting CA State Water Resources Control Board local oversight program (LOP) and CA Regional Water Quality Control Board LUST monitoring well data for MTBE and benzene in 58 counties, 29,000 wells; RWQCB #8: 84% of LUST releases have MTBE in ground water.

Estimated completion date June 1999  
Source Characterization; Occurrence

EPA-Region 9

Applicability of EPA Methods for MTBE analyses

Rich Bauer EPA-Reg.9, Richmond Lab

Applicability of EPA Methods 8020 and 8240, and 524.2 for drinking water analyses for MTBE.

Estimated completion date Sept. 1998

Occurrence (Analytic Methods)

EPA-Region 9

Database for Ground/surface Water Vulnerable to MTBE Contamination

Region 9 MTBE Cross-media Workgroup & Region 9 Ground Water Workgroup

(Matt Hagemann)

Compiling MTBE occurrence and source data for ground and surface water from State LUST programs, Drinking Water programs and TRI data. Documenting QA/QC for assembled data, presenting it in GIS layers, estimating vulnerability based upon established criteria, and evaluating need for further assessment in vulnerable areas in California, Nevada, Arizona, Hawaii, Pacific Islands, Tribal Lands.

Estimated completion date June 1999

Occurrence; Source Characterization

EPA-Region 9 / EPA-ORD

MTBE Exposure During Showering

Henry Lee, EPA-Reg9

*Proposal:* to measure air, blood, urine, and breath concentrations of MTBE in shower microenvironment; possibly include study of hedonic reactions in human subjects.

Estimated completion date June 1999

Exposure

European Union / Finnish Institute of Health

MTBE Risk Assessment

Contact?

Assessment of consumer and occupational health and environmental risks of MTBE

Publication expected in late 1998, early 1999

Assessment

Global Geochemistry Corporation

Gasoline Oxygenate Analysis in Environmental Samples by Two-dimensional Gas Chromatography

Yakov Galperin, Global Geochemistry Corporation

EPA methods (8020 and 8260) currently recommended for analyzing MTBE often lack adequate sensitivity for gasoline-rich samples. Modified ASTM D4815 method uses a two-dimensional gas chromatography system in which one column removes the hydrocarbons and the other separates the oxygenates with consequent detection by FID to

analyze MTBE, DIPE, ETBE, TAME, TBA, and methyl-, ethyl- alcohols in groundwater and soil.

Paper presented at West Coast Conference on Contaminated Soil and Groundwater, March 9-12, 1998

Occurrence (Analytic Methods)

International Agency for Research on Cancer

MTBE Monograph

Contact?

Evaluation of carcinogenic risks of MTBE to humans.

Workgroup review in late 1998; publication in 1999-2000?

Assessment

Johns Hopkins Univ.

Dermal Uptake of MTBE from Water

Tim Buckley, JHU

*Proposal:* to characterize dermal uptake of MTBE in water in human volunteers as a function of duration of exposure, volume of water, and concentration of MTBE.

Seeking funding

Health Effects

Lawrence Livermore National Lab / DOE / WSPA / CARB

MTBE Fate in Groundwater

Anne Happel, LLNL

Field study of >600 sites of MTBE-gasoline releases from USTs.

Final report due in March, 1998

Transport & Transformation

Lawrence Livermore National Lab / Calif. State Water Res. Bd. / U.S. DOE

Evaluation of Analytical Methods

Anne Happel, LLNL

EPA Methods 8020 and 8240 compared for false positives in GC/PID analyses for MTBE at field CA UST sites.

Completed; report available

Occurrence (Analytic Methods)

Lovelace / HEI

Toxicokinetics of MTBE With and Without Gasoline

Janet Benson, Lovelace / Maria Costantini, HEI

Quantify uptake, metabolism, and excretion of C-14 labeled MTBE alone and in gasoline over a range of concentrations and repeated inhalation exposures in rats.

Ongoing through 1998

Health Effects

Metcalf & Eddy / API  
Characterization of Service Station Stormwater Runoff  
Bruce Bauman, API  
Contractor to develop sampling plan to collect stormwater samples at several retail marketing facilities; samples to be analyzed for BTEX, MTBE, heavy metals and a variety of other parameters.  
Funded through 1998; draft report expected in late 1998  
Source Characterization; Occurrence

Metropolitan Water District of Southern Calif.  
Surface Water Sampling  
Marshall Davis, MWD  
Sampling for MTBE and other gasoline components in drinking water reservoirs used for recreational boating.  
Currently sampling; data collection started 1996; expected through 1998; report available in mid-1998  
Occurrence; Source Characterization

N.C. State Univ. / API  
Monitoring Degradation: Sampson Co., NC  
Robert Borden, NCSU  
Monitoring degradation of MTBE, BTEX in plume from LUST in shallow coastal aquifer in Sampson Co, NC; leak discovered ~1986, remediated 1990.  
One report completed; confirmation data to be included in final report in late 1998  
Transport & Transformation

National Research Council  
Intrinsic Remediation Study  
NRC Water Science and Technology Board  
Assessment of current scientific understanding of natural processes that degrade or immobilize contaminants, including oxygenates, in soil and groundwater.  
Draft expected in November, 1998  
Assessment

National Toxicology Program  
Proposed Listing of MTBE  
C.W. Jameson, NTP-NIEHS  
Call for public comments for proposed listing of chemicals, including MTBE, in "Report on Carcinogens, Ninth Edition" (Fed. Reg., Feb. 3, 1998 [63 FR 5565])  
Comment period closed  
Assessment

NESCAUM / Northeastern Univ.  
Comparative Gasoline Analysis  
Jason Grumet, NESCAUM

Comparative analysis of exposure and health impacts of oxygenated and nonoxygenated gasoline to consumers; targeted completion Dec 1997.

External review draft expected in spring, 1998

Assessment

Oregon Graduate Institute / API

Removal of MTBE from a Residual Gasoline Source Through in situ Air Sparging

Rick Johnson, OGI / B. Bauman, API

To assess: 1) effectiveness of in situ air sparging to remove MTBE from source zone; 2) extent to which such treatment results in reduction in MTBE in groundwater downgradient.

Underway; report expected in early 1999

Contaminant Removal; Transport & Transformation

Oregon Graduate Institute / Arizona State U. / API

Field Tracer Experiment at Port Hueneme, CA

Contact? / B. Bauman, API

Deuterated MTBE and tracer to be injected into existing MTBE plume to be followed by quarterly sampling for 1-2 years to determine changes attributable to biodegradation.

Underway; report expected in early 1999

Transport & Transformation

Oxygenated Fuels Assoc. / CIIT

Enforceable Consent Agreement for ETBE & TAME testing

John Kneiss, OFA / Susan Borghoff, CIIT

PBPK modeling for oral and inhalation exposures in rats to predict human PK.

Work being completed and reported in varying intervals, 1998

ETBE: Phase 1 (90-day toxicity study, neurotoxicity, genotoxicity, and inhalation PKs); Phase 2 (reproductive/developmental in 2 species).

Completed; some reports available; other reports expected in 1998

TAME: Phase 1 (mutagenicity, developmental completed; inhalation PKs, 90-day toxicity study, neurotoxicity, cell proliferation); Phase 2 (reproductive/fertility).

Work completed; some reports available; other reports expected in spring, 1998

Health Effects

Oxygenated Fuels Assoc. / CIIT

MTBE Cancer Mechanisms

John Kneiss, OFA / Susan Borghoff, CIIT

Voluntary study of role of alpha-2u-globulin in MTBE-induced kidney tumors in male rats.

Majority of work completed; report expected in fall, 1998

Health Effects

Regenesis Bioremediation Products

Commercial Technology for MTBE Degradation: ORC

Steve Konigsberg, California

Oxygen Release Compound (ORC, time-release magnesium peroxide) used in bioremediation of BTEX reported to work effectively in degrading MTBE also.

For more information see internet site - <http://www.regenesis.com/Tb2231.htm>  
Contaminant Removal

Rutgers Univ. / API  
Ex Situ Biological Treatment of Water  
R. Cowan, Rutgers / Bruce Bauman, API  
Development of technology to biologically treat MTBE-contaminated water ex situ.  
Underway through 1999; interim report expected in late 1998  
Contaminant Removal

Rutgers Univ. / HEI  
Role of Human Cytochrome P450 2E1 in Metabolism and Health Effects of Gasoline Ethers  
Jun-Yan Hong, Rutgers / Maria Costantini, HEI  
Characterize metabolism of MTBE and other ethers in human liver microsomes, with attention to  
role of CYP 2E1 and its genotypic distribution in humans; compare ether metabolism in  
human liver microsomes vs. rat and monkey nasal mucosa microsomes, to illuminate  
relevance of animal studies to humans.  
Ongoing through 1998  
Health Effects

Shell Development Corp.  
Polymer-solvent Interactions  
P. A. Westbrook, Shell Development Corp.  
Prediction of polymer/elastomer response to MTBE-gasoline blends based on response to neat  
MTBE.  
Status?  
Release Prevention

Shell Development Corp.  
MTBE Bioremediation  
J.P. Salanitro, Shell Development Corp.  
Isolation of bacterial culture capable of degrading MTBE in ground water.  
Ongoing  
Contaminant Removal; Transport & Transformation

State of Calif. Dept. Health Services, Division of Drinking Water / EPA-Region 9  
Monitoring Drinking Water Sources: California  
David Storm - CA DHS / Bill Robberson - EPA-Region 9  
Monitoring for MTBE in drinking water sources statewide  
Ongoing; data available on-line (<http://www.dhs.cahwnet.gov/org/ps/ddwem>)  
Occurrence

State of Calif. / Univ. Calif.  
Senate Bill 521 Studies  
Jerold Last, UC-Davis

The California State Legislature recently passed Senate Bill 521 appropriating funds to the University of California, mandating specific areas of study (tasks) and deadlines for reports of results. Awards totaling \$500K were made as follows (task numbers refer to original RFP):

1. Evaluation of the Peer-reviewed Research Literature on the Human Health, including Asthma, and Environmental Effects of MTBE, John Froines, UCLA, \$99,000, tasks #1 (health effects), #8 (asthma-specific survey of health effects), #10 (literature review of health effects).
2. Integrated Assessment of Sources, Fate & Transport, Ecological Risk and Control Options for MTBE in Surface and Ground Waters, with Particular Emphasis on Drinking Water Supplies, John Reuter and Daniel Chang, UCD, \$220,000, tasks #3 (environmental and ecological effects of MTBE), #4 (current levels of MTBE in water), #5 (treatment technologies for MTBE removal from water), #6 (impact of MTBE on vehicles), #7 (corrosive effects of MTBE on storage tanks), #11 (Lake Tahoe Basin assessment), and #12 (integrative summary).
3. Evaluation of Costs and Effectiveness of Treatment Technologies Applicable to Remove MTBE and Other Gasoline Oxygenates from Contaminated Water, Arturo Keller, UCSB, \$49,000, task #5 (remediation technologies).
4. Drinking Water Treatment for the Removal of Methyl Tertiary Butyl Ether from Ground Waters and Surface Water Reservoirs, Irwin Suffet, UCLA, \$49,000, task #5 (remediation technologies).
5. Evaluation of MTBE Combustion Byproducts in California Reformulated Gasoline, Catherine Koshland, UCB, \$49,930, task #9 (combustion byproducts of MTBE).
6. Risk-based Decision Making Analysis of the Cost and Benefits of MTBE and Other Gasoline Oxygenates, Arturo Keller, UCSB, \$33,070, task #12 (integrative summary).

Studies due to Governor by January 1, 1999; interim report by July, 1998; final reports by October, 1998  
Assessment

U.S. Geological Survey - NAWQA  
National Retrospective Analyses: Selected Areas  
John Zogorski, Wayne Lapham, USGS  
Retrospective analysis of VOC and limited MTBE data in about 20 U.S. areas: CA, ID, IA, NJ, NY, TX, WI; several other areas available for further analyses; additional data being sought for 1998 - 1999.

Ongoing through 2000; findings published yearly  
Occurrence; Source Characterization

U.S. Geological Survey - NAWQA  
Groundwater Monitoring: Michigan (1996 - 1998)  
Mary Ann Thomas, USGS  
Characterization of groundwater in residential suburban Detroit area; preliminary data analysis did not indicate presence of MTBE or TBA.  
Monitoring nearly completed; data release expected in mid-1999  
Occurrence; Source Characterization

U.S. Geological Survey - NAWQA

Transport & Fate: Glassboro, NJ (Glassboro Comprehensive Urban Study)

John Zogorski, Arthur Baehr, Mark Ayers, USGS

Monitor MTBE, VOCs in air, precipitation, surface water (streamflow, stormwater), unsaturated zone (vapor/sediments, core analysis, modeling movement/loading to water table), ground water (shallow/deep monitoring, modeling of flow, transport & fate) in Glassboro, NJ (Kirkwood-Cohanwey Aquifer Syst.).

Ongoing 1996-2000; project description published; shallow ground-water VOC data published; research published periodically

Transport & Transformation; Source Characterization

U.S. Geological Survey - NAWQA

Monitoring Urban Storm Water: Selected Areas

John Zogorski, USGS

Monitor urban storm water for VOCs, including MTBE, in 16 U.S. metropolitan areas: Boise, Phoenix, Colo. Springs, Denver, San Antonio, Dallas, Omaha, Independence, Little Rock, Davenport, Baton Rouge, Mobile, Huntsville, Birmingham, Montgomery, Atlanta.

Compilation completed; occurrence report completed; some USGS districts still collecting storm water data; no further national compilation planned

Occurrence; Source Characterization

U.S. Geological Survey - NAWQA / EPA-OW

Retrospective Analyses: New England-Mid Atlantic (12 states)

Steve Grady, USGS / Mike Osinski, EPA-OW

Retrospective data analysis for MTBE and other VOCs in ground/drinking water in 12 southern New England and Mid-Atlantic states. Focus primarily on ambient ground water and PWS drinking water data for MTBE and other VOCs, with one of the objectives being to create a protocol to be used in obtaining state drinking water quality data. Protocol development to address minimum data elements needed to describe water sources (location, well characteristics, geology, well log info, etc.) and lab methods, MDL, etc. used for the SAR.

Design completed; retrospective started; report due late 1999

Occurrence; Source Characterization

U.S. Geological Survey - NAWQA / Oregon Graduate Institute

Plant Transpiration

John Zogorski, USGS / Jim Pankow, OGI

Measurement of plant transpiration on VOC levels including MTBE.

Preliminary study planned for late 1998; report and journal article planned for 1999

Transport & Transformation

U.S. Geological Survey - NAWQA / Oregon Graduate Institute

VOC Behavior and Fate

John Zogorski, USGS, Jim Pankow

Modeling the behavior and fate of VOCs including MTBE in PWS reservoirs.

Model to be developed in 1998; journal article and documentation report planned in 1999  
Transport & Transformation

U.S. Geological Survey - NAWQA / Oregon Graduate Institute

VOC Analytic Methods: Air

John Zogorski, USGS / Jim Pankow, OGI

Analytic methods developed for VOCs, including MTBE, TAME, DIPE, and ETBE, in ambient  
air.

Report to be prepared in 1998

Occurrence (Analytic Methods)

U.S. Geological Survey / Oregon Graduate Inst.

Degradation Assessment

John Zogorski, USGS / James Pankow, OGI

Determine degradation pathways, by-products, kinetics, and their relationship to varied geological  
environments for MTBE, TBA, TBF, TAME, TAA, and acetone based on monitoring data  
from several plumes and lab studies.

Field monitoring and lab studies continuing in 1998; project findings and lab analytical method  
published; research findings published periodically

Transport & Transformation

U.S. Geological Survey / Oregon Graduate Inst.

Modeling Non-point Source Inputs

John Zogorski, USGS / James Pankow, OGI

Modeling of atmospheric and land-based non-point source inputs of MTBE to ground water  
systems (see also USGS: Glassboro, NJ study under Transport & Fate).

Ongoing 1996-2000; research published periodically

Source Characterization; Occurrence; Transport & Transformation

U.S. Geological Survey - Toxics Hydrology Program

Monitoring Plume: Beaufort, SC

Herb Buxton, John Zogorski, J. Landmeyer, USGS

Ongoing monitoring of shallow ground water and unsaturated zone above the ground water plume  
for VOCs, including MTBE, BTEX, TBA, for movement and degradation since 1991 at  
Laurel Bay UST (Beaufort Marine Corps Air Station, SC); remediated 1993; flow and  
contaminant modeling; long-term hydrology study site.

Ongoing; project scope and findings through 1997 published; research published periodically

Transport & Transformation

Univ. Calif. - Davis

Sources, Fate and Transport of MTBE in Sierra Nevada Multiple Use Lakes

John E. Reuter, UC-D

Study of sources, transport and fate of MTBE in Lake Tahoe and Donner Lake.

Ongoing

Transport & Transformation; Source Characterization

Univ. Calif. -Davis / API

Vapor Phase Biodegradation of MTBE

E. Schroeder, UC-Davis ; B. Bauman, API

To evaluate the effectiveness of biofilters in MTBE vapor phase treatment; culture aerobic, naturally occurring microbial consortium that rapidly degrades MTBE, uses MTBE as its sole carbon and energy source, and has been shown (Eweis et al., Proceedings 90<sup>th</sup> AWMA Meeting, Toronto, June 8-13, 1997) to degrade MTBE in both liquid and gas streams (biofilters); assess impact of other organics (e.g., aromatics, alkanes) on MTBE biodegradation; characterize potential limitations of technology.

Nearly completed; report expected in Fall, 1998

Contaminant Removal

Univ. Houston / API

Characteristics of MTBE from a Gasoline Source

William G. Rixey, U. Houston / B. Bauman, API

To characterize dissolution and desorption of MTBE from a gasoline source residually trapped in soil; information to be used to assess duration of MTBE in source area. Leaching behavior to be evaluated in laboratory fixed-bed columns and results modeled.

Currently collecting data; draft report due in late 1998

Transport & Transformation

Univ. Mass - Amherst / EPA-OUST

Survey of States for Lust-MTBE Impacts

Paul Kostecki, U.Mass-Amherst / R. Hitzig, EPA-OUST

Survey of state agencies regarding numbers of sites with MTBE releases, numbers of impacted private and public drinking water wells, remediation methods, and regulations.

Underway; draft of report due in April, 1998

Occurrence; Contaminant Removal

Univ. Mass. - Amherst / API

Anaerobic Degradation of MTBE, BTEX, and PAHs in Petroleum-Contaminated Aquifers

Derek Lovley; Univ. Massachusetts-Amherst / B. Bauman, API

To determine: 1) potential for ferric iron to serve as electron acceptor for anaerobic biodegradation of MTBE and BTEX in groundwater and rates associated with this process in variety of aquifers; 2) anaerobic processes in the source area of fuel spills; 3) anaerobic biodegradability of PAHs in groundwater.

Underway; report expected in early 1999

Transport & Transformation; Contaminant Removal

Univ. Michigan

MTBE Behavior in BTEX Plume

Mike Barcelona, Univ. Michigan

MTBE behavior after injection in a BTEX plume assessed from initial release.

Funding commitment uncertain; plan to sample April, 1998 - October, 1999

Transport & Transformation

Univ. Nevada - Reno  
Sampling for MTBE in Lake Tahoe  
Glenn Miller, UN-R  
Sampling for MTBE from various depths and locations, including temperature and meteorology data; volatilization models to be run.  
Currently sampling through 1998; funding in 1999 less certain  
Occurrence; Source Characterization; Transport & Transformation

Univ. Northern Iowa / Exxon  
Effect of MTBE on Microbial Consortia  
C. M. Horan, Univ. N. Iowa  
MTBE added to microbial consortia increased oxygen consumption, but concs. up to 740 mg/L inhibited mineralization potential of hexadecane up to 50%; although MTBE can be metabolized in environment, toxicity may adversely affect overall biodegradation of fuel HCs.  
Ongoing; published report in 1997  
Contaminant Removal; Transport & Transformation

Univ. Notre Dame / Amoco Corp.  
MTBE Biodegradation by Pure Cultures  
Charles Kulpa, Univ. Notre Dame  
Isolation of pure and mixed bacterial strains capable of degrading MTBE in soil and water  
Ongoing; published report (Appl. Microbiol. Biotechnol. 47:69-72, 1997).  
Contaminant Removal; Transport & Transformation

Univ. Texas - Austin / API  
Spatial and Temporal Variability of MTBE Plumes in Texas  
Robert Mace, U. Texas-Austin / B. Bauman, API  
To characterize spatial and temporal variation of MTBE plumes and their relation to other dissolved hydrocarbons, the nature of the release source, and site hydrogeology using existing database of 361 Texas UST sites.  
Draft report expected in summer, 1998  
Transport & Transformation

Univ. Waterloo / API  
Monitoring Plume: Waterloo, Ont.  
Jim Barker, Univ. of Waterloo  
Monitoring of MTBE, BTEX, MeOH, NaCl in experimental plume at Canada Forces Base Borden, Ontario; began ca. 1988, tracked for 16 months, resumed in 1996.  
Nearly completed; report due in spring, 1998; monitoring ongoing  
Transport & Transformation

Univ. Waterloo / API  
MTBE Natural Attenuation Field Research, Phase 1  
Doug Mackay, U. Waterloo / B. Bauman, API

To identify suitable research site and generate initial site characterization data to determine:  
1) mass flux of MTBE from a release site and its influence on the size of the resultant dissolved phase plume; and 2) natural attenuation processes that act to limit the migration of dissolved MTBE at that site.

Ongoing through 2001; interim reports expected annually  
Transport & Transformation

Univ. Wurzburg / HEI

Comparative Biotransformation of MTBE, ETBE, TAME, and DIPE in Rats and Humans  
Wolfgang Dekant, Wurzburg / Maria Costantini, HEI

Compare relative excretion of ether metabolites in humans and rats exposed in vitro and in vivo via inhalation, with attention to individual differences.

Ongoing through 1998

Health Effects

Western States Petroleum Association

Well Purging Study: California

Jeff Sickenger, WSPA

Comparison of MTBE, BTEX, and TPH-g in groundwater samples before and after purging at CA wells: concs. higher before than after purging, variability of before/after concs. comparable to variability between purging methods; high variability in small pop. of sites due to site-specific conditions.

Status?

Contaminant Removal; Transport & Transformation

World Health Organization - IPCS

Environmental Health Criteria for MTBE

Edward Smith, WHO Geneva

Draft completed; publication expected in Spring, 1998

Assessment