

# **HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

**REPORT TO THE GOVERNOR AND  
LEGISLATURE OF THE STATE OF CALIFORNIA  
AS SPONSORED BY SB 521**

**VOLUME I  
SUMMARY & RECOMMENDATIONS**

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## INTRODUCTION

To address the questions posed by SB 521, the University of California conducted a competitive peer reviewed request for proposals. A total of six grants were selected for funding. Between them, these six proposals cover essentially the entire range of mandated tasks as specified in SB521 and in the RFP. The successful grants are listed below by Title, Principal Investigator(s), UC Campus receiving the award, and task(s) to be covered.

1. *An Evaluation of the Peer-reviewed Research Literature on the Human Health, including Asthma, and Environmental Effects of MTBE*  
John Froines, Ph.D., UCLA  
Tasks: 1 (health effects), 8 (asthma-specific survey of health effects), 10 (literature review of health effects), and portions of task 2
2. *An 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, Ph.D. and Daniel Chang, Ph.D., UCD  
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, Ph.D., UCSB  
Task: 5 (remediation technologies)
4. *Drinking Water Treatment for the Removal of Methyl Tertiary Butyl Ether from Ground Waters and Surface Water Reservoirs*  
Irwin (Mel) Suffet, Ph. D., UCLA  
Task: 5 (remediation technologies)
5. *Evaluation of MTBE Combustion Byproducts in California Reformulated Gasoline*  
Catherine Koshland, Ph.D., UCB  
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, Ph.D. and Linda Fernandez, Ph.D., UCSB  
Task: 12 (integrative summary)

Total amount awarded to investigators: \$500,000. None of the total SB521 appropriation was spent on administrative costs for the peer-review process.

Further details are available on the TSR&TP website at: <http://tsrtp.ucdavis.edu/>

## **SB 521 RESEARCH TOPICS**

**The mandated research topics specified in SB 521 are as follows:**

1. An assessment of the risks and benefits to human health and the environment of MTBE and its combustion byproducts found in air, water, and soil, and a comparison of those risks and benefits to ETBE, TAME, and ethanol that could be used in lieu of MTBE in gasoline.
2. An assessment of available research and data on the impact of MTBE on human health and the environment in each state where MTBE has been used in gasoline at levels of 10 percent or greater, by volume, within the last five years.
3. An assessment of the risks to human health and the environment associated with MTBE leaking from underground and aboveground storage tanks, from surface watercraft and other sources of MTBE pollution in surface water bodies, and from oceangoing tankers in coastal waterways of this state.
4. An analysis of current levels of MTBE in the state's drinking water, reservoirs, lakes, and streams.
5. An evaluation of the costs and effectiveness of treatment technologies available to remove MTBE from surface waters, groundwaters, and drinking water.
6. An assessment of the impact of MTBE on vehicle parts and the efficient operation of vehicles.
7. An assessment of the corrosive effects of MTBE on the structural integrity of fiberglass storage tanks, which may be undertaken in consultation with the California Fire Chiefs Association and other recognized experts on the matter.
8. A comparison of the incidence of asthma before and after the level of MTBE was increased in California gasoline, considering appropriate factors relating to a nexus between any change in the incidence of asthma and the actual introduction of MTBE into California gasoline.
9. Identification and quantification of all of the combustion byproducts of MTBE in California's reformulated oxygenated fuel and the type of analytical methods used and their sensitivity.
10. An evaluation of the scientific peer-reviewed research and literature on the human health and environmental effects of MTBE, as well as any original research necessary to provide the information specified in paragraphs (1) to (9), inclusive.
11. A focused assessment of the subjects provided for in paragraphs (1), (3), (4), (5), and (8) for the Lake Tahoe Basin.
12. In addition to the 11 areas specified above, the UC TSR&TP specifically wished to address integration of the scientific information obtained by investigators funded by this program, and develop a set of policy options for the legislature, based insofar as possible on sound scientific principles and cost-benefit analysis.

## EXECUTIVE SUMMARY & RECOMMENDATIONS

The use of California Phase II Reformulated Gasoline (CaRFG2) since June of 1996, has resulted in reductions in the emissions of various air pollutants including benzene, a known human carcinogen. These reductions in pollutant emissions can be translated into human and environmental health benefits. Meeting the CaRFG2 requirements to achieve these air quality benefits, however, incurs additional costs to manufacture reformulated gasoline. The additional fuel cost is paid by consumers at the pump as a net increase in fuel price, and as decreased fuel efficiency due to the lower energy content of gasoline with oxygenate. We estimate this cost to be on the order of \$590 million to \$1.4 billion per year for California. In addition, CaRFG2 and Federal Reformulated Gasoline (RFG) must, as mandated by Federal law, contain a certain percentage of oxygen content in designated non-attainment areas. These oxygenate compounds can contaminate water sources, and also result in air emissions specific to these additives.

Beginning in the late 1980s studies were undertaken to identify ways in which gasoline could be reformulated to help achieve certain air quality goals. Based on studies with older vehicles, it was determined that adding oxygenated organic compounds, such as alcohols and ethers to conventional gasoline, resulted in a reduction in the emissions of carbon monoxide and other products of incomplete combustion. Subsequent studies identified several ways in which gasoline could be reformulated. Compared to conventional gasoline, RFG has reduced vapor pressure (to lower evaporative emissions), reduced sulfur content (to prevent poisoning of catalytic converters), and reduced aromatic and benzene content (to decrease evaporative and exhaust emissions of these compounds). Reformulated fuel may or may not include oxygenated compounds; the term “reformulated gasoline” does not itself imply the presence of oxygenates.

There are two primary types of RFG: Federal RFG and California Phase 2 RFG. Federal RFG requires a minimal oxygen content of 2.0 wt%, but does not specify what type of oxygenate must be used. CaRFG2 specifies an oxygen content of 1.8 to 2.2 wt%, with no mandate for any particular oxygenate.

The CaRFG2 standard may be met: (1) by meeting the prescriptive limits, or (2) by using a predictive model to show that emissions reductions achieved using a given fuel formulation are equivalent to, or greater than, those achieved using the prescriptive fuel formula. Gasoline refiners are free to use any of the various oxygenates to meet RFG and CaRFG2 oxygen content requirements in California, and have used MTBE, other ethers, and ethanol for this purpose. Most refiners have chosen to use MTBE. In air basins that meet the National Ambient Air Quality Standards (“attainment areas”), non-oxygenated CaRFG2 may be sold.

In comparison to conventional gasoline, RFGs show significant improvement on several measures of air quality. Emissions of carbon monoxide, volatile organic compounds, and nitrogen oxides are reduced with CaRFG2 as compared to conventional gasoline. Vehicle emission control technology, especially improvements in newer cars, also significantly reduce emissions of air pollutants and their precursors. **MTBE and other oxygenates were found to have no significant effect on exhaust emissions from advanced technology vehicles. There is no statistically significant difference in the emissions reduction of benzene between oxygenated and non-oxygenated RFGs that meet all other CaRFG2 standards. Thus, there is no significant additional air quality benefit to the use of oxygenates such as MTBE in reformulated gasoline, relative to alternative CaRFG2 non-oxygenated formulations.**

There are significant risks and costs associated with water contamination due to the use of MTBE. MTBE is highly soluble in water and will transfer readily to groundwater from gasoline leaking from underground storage tanks, pipelines and other components of the gasoline distribution system. In addition, the use of gasoline containing MTBE in motor boats, in particular those using older 2-stroke engines,

results in the contamination of surface water reservoirs. The extent of MTBE contamination is discussed in more detail in Section 5, but it is clear we are placing our limited water resources at risk by using MTBE. MTBE has been detected in several water supply systems, which have shut down the contaminated sources, resorting to alternative supplies or treatment. Since both groundwater wells and surface water reservoirs have been contaminated, alternative water supplies may not be an option for many water utilities. **If MTBE continues to be used at current levels and more sources become contaminated, the potential for regional degradation of water resources, especially groundwater basins, will increase. Severity of water shortages during drought years will be exacerbated.**

For the general population, the risk of exposure to MTBE through ingestion of MTBE-contaminated water is currently low. CAL-DHS has set up a monitoring program of public drinking water supplies, which will result in detection of MTBE-contaminated sources before most California residents are exposed. Large water utilities will likely shut down contaminated water sources to avoid supplying water even at the 5ug/L level, seeking alternative water sources, at an additional cost to the consumers or to taxpayers. People supplied by small public water systems or private drinking water supplies are most likely to be exposed to MTBE, since they are not required to monitor water quality. Many individuals do not taste or smell MTBE at the 5 ug/L level, and thus may be exposed to higher concentrations for a significant amount of time. In Section 6 we evaluate possible exposure scenarios. MTBE exposure through inhalation is likely to be below health-threatening levels, except for occupational workers such as gasoline station attendants and auto mechanics. It should be stressed, however, that there are important data gaps in our understanding of the acute and chronic toxicity of MTBE. Little or no research is currently being conducted that directly addresses these issues. Section 3 discusses areas of potential concern including risks of cancer, asthma, neurologic, reproductive, and developmental effects, taste and odor thresholds, and possible acute effects at low concentrations.

The cost of treatment of MTBE-contaminated drinking water sources in California could be enormous. In addition, the cost of remediating Underground Storage Tank (UST) and pipeline leaks and spills could be on the order of tens to hundreds of millions of dollars per year. There are other significant costs to the economy, which may be in the tens of millions of dollars per year, in terms of monitoring of surface water sources for MTBE and potential losses in recreational income to surface water reservoirs that ban or restrict the use of gasoline-powered boats. We believe that the use of either non-oxygenated reformulated gasoline or ethanol as an oxygenate in CaRFG2 would result in much lower risk to water supplies, lower water treatment costs in the event of a spill of either of these alternative RFG formulations, and lower monitoring costs.

In Section 9 we present an economic analysis of the benefits and costs associated with three gasoline formulations: CaRFG2 with MTBE, CaRFG2 with ethanol, and CaRFG2 without added oxygenate. The cost benefit analysis indicates that non-oxygenated gasoline achieves air quality benefits at the least cost, followed by CaRFG2 with ethanol. CaRFG2 with MTBE has a net annual cost of \$1-3 billion, due primarily to the costs of treating contaminated water supplies, higher fuel prices, lower fuel efficiency, and is the most expensive alternative. From a purely economic perspective, it would be best to transition to non-oxygenated CaRFG2. However, fuel oxygenate content is mandated by federal law, and this may not be a viable option. **In addition, a lesson to be learned from the MTBE story is that addition of any chemical compound to the environment in quantities that constitute a significant fraction of the total content of gasoline may have unexpected environmental consequences. Therefore, we recommend a full environmental assessment of any alternative to MTBE in CaRFG2, including the components of CaRFG2 itself, before any changes are made in California State law.**

Many communities around California have decided they would rather not be exposed to the risk of MTBE-contaminated water and are seeking to ban the use of MTBE in gasoline. An immediate ban of MTBE

will result in a significant disruption in gasoline production, possibly reducing the level of production from California refineries and driving up the price of gasoline paid by consumers. Some ethanol production capacity is immediately available, but to meet the expected increase in ethanol demand, California would have to bid away ethanol from the Midwest or resort to imports, which may involve significantly higher gasoline prices. Most refiners in California are not prepared to immediately produce only non-oxygenated RFG, and its use would not meet Federal RFG requirements for ozone non-attainment areas: Los Angeles, Orange, Riverside, Ventura, San Bernardino, Imperial, San Diego and Sacramento Counties.

**Rather than any immediate ban on MTBE, we recommend consideration of phasing out MTBE over an interval of several years, and that refiners be given flexibility to achieve CARB's air quality objectives by modifying the caps in the CaRFG2 specifications to allow wide-scale production of non-oxygenated RFG. Using CARB's Predictive Model as a guideline, refiners can find the most cost-effective formulation for each region and season, without assuming the liability and risks that MTBE poses to California's water supplies.**

During the transition phase, a number of policies are suggested to reduce the cost of using MTBE while protecting water supplies. These policies are:

1. Restrict the use of CaRFG2 with MTBE to ozone non-attainment areas during the summer months. It is recommended that CARB review the length of the ozone summer season for those air basins in non-attainment, to limit as much as possible the use of CaRFG2 with oxygenates.
2. Obtain a waiver of the Federal requirement that RFG sold in California have an oxygen content, via the passage of HR Bill 630 and Senate Bill 1576. This will allow the sale of non-oxygenated CaRFG2 in all areas.
3. Recommend that CARB facilitate promotion of the production and distribution of non-oxygenated CaRFG2 in all attainment areas, as well as during the non-summer season in non-attainment areas.
4. Promote the accelerated removal of older, high emitting motor vehicles through the use of industrial emissions offsets or a fund created by an appropriate tax. This program would be significantly more cost-effective than mandating the use of oxygenates in fuels in reducing air pollutant emissions. An aggressive program aimed at gross CO polluters would be a cheaper and less risky option than using oxygenates.
5. Maintain the Underground Storage Cleanup Fund Program, possibly beyond the year 2005 to cover the costs of MTBE cleanup, with a review in 3 years to determine the effectiveness of upgraded underground storage tank systems in reducing the rate of failures, and thus the potential to reduce the annual fees.
6. Where contamination of groundwater is known or suspected, evaluation of plume extent and potential threats to drinking-water supply wells should be carried out immediately. Plume containment, remediation, or other corrective actions should then proceed as soon as possible to reduce risk and costs.
7. Require the adoption of Best Management Practices for surface water reservoirs, following the lead of the Santa Clara Valley Water District.

8. Establish specific emissions requirements for motor boat engines, in particular with respect to emissions of unburned fuel. Promote legislation with incentives to phase out motor boat engines that do not meet emissions requirements.
9. Assess the environmental impacts of using other oxygenates such as ethanol. **It must be stressed, however, that there are potential adverse health effects associated with incomplete combustion products of ethanol, and further study of combustion byproducts and potential health effects of such products is required before substitution of ethanol for MTBE on a large scale can be recommended.** If ethanol is found to provide a net energy savings and have minimal environmental impacts, then, increase the availability of ethanol as a potential oxygenate, by increasing the use of agricultural wastes such as rice straw for ethanol production. This also would reduce the emissions from burning the rice straw. The increase in this program could be funded through reductions in the cost of monitoring and enforcing the ban of rice straw burning.
10. The State should invest in a long-term research program, using the enormous base of expertise available in California's universities and professional organizations, to determine the toxicological effects of untested industrial products that will be used in large amounts. Such research should, for example, examine effective alternatives for motor vehicle fuels, and develop more cost-effective remediation and treatment technologies. The current structure of State Agencies, which focus on specific media (land, air, water), leads to fragmented and incomplete environmental impact assessments. Any new large scale programs in California should be preceded by an independent Environmental Impact Assessment, rather than an *a posteriori* evaluation of the consequences.

# SUMMARY

## 1. BACKGROUND

California Senate Bill 521 (SB 521), enacting the MTBE Public Health and Environmental Protection Act of 1997, signed into law on October 8, 1997, directed the University of California to conduct research on the effects of the gasoline additive Methyl *tertiary*-Butyl Ether (MTBE). This report summarizes the findings and opinions of a multi-disciplinary group of scientists from the UC system with respect to the complex set of issues surrounding the use of gasoline additives such as MTBE to reduce air pollution, given the negative impact these additives can have on water resources.

The use of MTBE in California Phase II Reformulated Gasoline (CaRFG2) is not mandated by state regulations, but MTBE has become the oxygenate of choice among the state's refiners, mostly due to economic considerations. MTBE was first used in U.S. gasoline in 1979, primarily in premium grades of gasoline at levels of 2 to 3% by volume, as an octane booster and replacement for lead in gasoline. Currently, MTBE constitutes approximately 11% by volume of California gasoline. Statewide, about 100,000 barrels of MTBE are consumed each day. MTBE has been used at these levels since June 1996, when CaRFG2 requirements became effective. While SB 521 is specifically geared towards an evaluation of MTBE itself, it is imperative to evaluate MTBE in the context in which it is currently used in California, as a component of CaRFG2. It is important to understand what reformulated gasoline is, as well as its intended and actual effects on automotive emissions and ambient air quality. Thus, several definitions are in order.

Oxygenates are organic molecules that contain oxygen. Oxygenates are typically alcohols (such as ethanol) or ethers (such as MTBE). The main purpose for adding oxygenates to fuels is to promote more efficient combustion under adverse conditions in the engine, such as cold starts or fuel-rich operations, when a substantial amount of fuel may escape the engine unburned. The extra oxygen in the fuel helps to convert carbon monoxide (CO, a product of incomplete combustion) to carbon dioxide. To a lesser extent, the extra fuel-bound oxygen may help to convert hydrocarbons, also formed as products of incomplete combustion, to carbon dioxide and water. Currently, the most widely used gasoline oxygenates in California are MTBE, ethanol, and *tert*-amyl methyl ether (TAME). In the San Francisco Bay Area in 1997, MTBE was found to constitute about 95% of the oxygenates used in gasoline (Kirchstetter et al., 1998a). Other oxygenates used to a much lesser extent include other ethers, such as ethyl *tert*-butyl ether (ETBE). In a few California markets, CaRFG2 is currently being marketed without added oxygenates.

**Oxyfuels** are oxygenated fuels that contain oxygenates at concentrations on the order of 10 to 15% by volume. Oxyfuels are used in urban areas during winter months to help reduce automotive CO emissions that cause ambient air quality problems. The Federal Clean Air Act Amendments of 1990 (CAAA) mandated the use of oxygenated fuels during winter months in approximately 40 urban areas throughout the U.S. that did not meet ambient CO standards. In these designated "non-attainment" areas, gasoline sold in the winter months must contain at least 2.7% by weight (wt%) oxygen, effective November 1992. California is exempted from this minimum oxygen level, because of concerns that this oxygen level would exacerbate state air quality problems by increasing automotive emissions of oxides of nitrogen (NO<sub>x</sub>). Thus, California's oxyfuel requirement was amended to require 1.8 to 2.2 wt% oxygen. 2.7 wt% oxygen corresponds to 15% by volume MTBE (or 7.3% by volume ethanol), while 2.0% oxygen corresponds to 11% by volume MTBE

(or 5.4% by volume ethanol). The Clean Air Act does not specify which oxygenate must be used.

**Conventional gasoline** refers to gasoline used nationwide before 1995. Conventional gasoline typically does not contain any oxygenates, except in quantities of about 2 to 3% by volume, when refiners have chosen to add them as octane boosters. Conventional gasoline typically has higher benzene content than reformulated gasoline.

**Reformulated gasoline** (RFG) differs from conventional gasoline with respect to several fuel parameters. RFG is intended to reduce automotive pollutant formation, especially evaporative emissions and exhaust emissions of photochemical ozone precursors. The most important targeted ozone precursors are volatile organic compounds (VOCs). RFG is also intended to reduce air toxic emissions, specified in the CAAA as benzene, 1,3-butadiene, formaldehyde, and acetaldehyde. Compared to conventional gasoline, RFG has reduced vapor pressure (to lower evaporative emissions), reduced sulfur content (to prevent poisoning of catalytic converters), and reduced aromatic and benzene content (to decrease evaporative and exhaust emissions of these compounds). Reformulated fuel may or may not include oxygenated compounds; the term “reformulated gasoline” does NOT itself imply the presence of oxygenates.

There are two primary “flavors” of RFG: Federal RFG and California Phase 2 RFG. Requirements for **Federal RFG** are defined in the CAAA. Federal RFG specifies maximum limits on vapor pressure, benzene content, and aromatics content; it prohibits any lead, requires detergents, and requires a minimal oxygen content of 2.0 wt%. Federal RFG does not specify what type of oxygenate must be used. Federal RFG also must meet a 15% reduction in air toxic and VOC emissions compared to conventional gasoline (25% emission reductions will be effective in 2000). Effective January 1, 1995, Federal RFG is required year-round in nine different areas in the U.S. with ozone levels classified as “severe” or “extreme.” In California, these areas include key population centers such as Los Angeles, San Diego, and Sacramento.

**California Phase 2 RFG** (CaRFG2, sometimes referred to as “Cleaner Burning Gasoline”) is required year-round, statewide, effective April, 1996. This regulation was enacted by the California Air Resources Board (ARB) as part of California’s State Implementation Plan under the CAAA to meet California air quality goals. CaRFG2 contains stricter provisions than Federal RFG, including restrictions on maximum sulfur content, aromatics content, altered distillation profile (to reduce evaporative emissions), and reduced olefin content (to reduce the reactivity of the exhaust hydrocarbons). CaRFG2 must also reduce automotive air toxic and VOC emissions by 25% compared to conventional gasoline. The “formula” for CaRFG2 specifies an oxygen content of 1.8 to 2.2 wt%, with no mandate for any particular oxygenate.

The CaRFG2 standard may be met in one of two ways: (1) by meeting the prescriptive limits, or (2) by using a predictive model to show that emissions reductions achieved using a given fuel formulation are equivalent to, or greater than, those achieved using the prescriptive fuel formula. Thus, if a refiner can show that a particular gasoline formulation that contains no oxygenates achieves the mandated emission reductions, that fuel formulation is allowed under the “predictive modeling” rules. Evaluation of gasoline sold in the San Francisco Bay Area indicates that usage of MTBE in Bay Area gasoline dropped by over 20% from 1996 to 1997 (from an average of 10.7 volume % MTBE in 1996 to an average of 8.2% in 1997). At the same time, the average oxygen content decreased by 20%, suggesting a corresponding increase in the use of non-oxygenated CaRFG2 (Kirchstetter et al., 1998a). Federal RFG requirements, including the minimum 2.0 wt% oxygen content, supersede state requirements only in federally-designated ozone non-attainment areas.

An adequate Environmental Impact Assessment of the potential effects of Federal RFG and CaRFG2 standards, with their requirement for oxygen content, would have shown that oxygenates are typically quite soluble in water, and thus very likely to impact water resources. In addition, knowing that MTBE was a likely choice of oxygenate and that these rules would cause a significant increase in the production and

use of this chemical, adequate toxicological and environmental research should have preceded the wide-scale introduction of oxyfuels. Even several years after MTBE's large-scale introduction, the human health and environmental impact information is incomplete. What we do know is that MTBE is quite persistent in the environment, and given its high solubility, its tendency to move as fast as the groundwater, and its tendency to not biodegrade as much as petroleum hydrocarbons, it is capable of contaminating water resources faster than any other gasoline component. In addition, the particular taste and odor properties of MTBE-contaminated water led US EPA, CAL-EPA, CAL-SWRCB and CAL-DHS to take steps towards controlling the spread of contamination. Subsequent review of existing toxicological information led to the establishment of a Public Health Goal (CAL-EPA, 1998) and the listing of MTBE as a potential human carcinogen in California. The following sections summarize our findings with respect to the human and ecological effects of MTBE, its combustion byproducts and metabolites, the extent of MTBE contamination in California, an exposure assessment under various scenarios, the cost of water treatment, and an integral cost-benefit analysis of the use of reformulated gasoline. We also present an economic evaluation of the cost of various policy options that can mitigate the impact of MTBE or promote alternative solutions.

## **2. AIR QUALITY BENEFITS OF REFORMULATED GASOLINE**

Air pollution from automobiles consists of both evaporative emissions and exhaust (tailpipe) emissions. Evaporative emissions of unburned gasoline occur during refueling or from fuel spills, as well as directly from the automobile itself from carburetors and other fuel system components. Evaporative emissions are a function of gasoline volatility. Exhaust emissions are a function of combustion conditions in the engine and activity of the catalytic converter. Exhaust emissions include unburned or partially oxidized hydrocarbons and NO<sub>x</sub>, which together are critical precursors in the formation of ozone. While it is difficult to make exact correlations between automotive emissions and ambient pollutant concentrations, particularly of secondary pollutants such as ozone, we know that automobile emissions have a major impact on air quality. Several types of studies are used to evaluate automotive emissions, including engine dynamometer tests conducted in laboratories using the Federal Test Procedure (FTP), intended to mimic a range of real-world driving conditions. More realistic estimates of in-use vehicle emissions are gathered from on-road studies or tunnel measurements.

It is important to distinguish the automotive emission reduction benefits that are associated with the use of oxygenated fuels from those associated with reformulated fuels. Our study evaluated these impacts by analyzing previous automotive and laboratory studies, as well as extensive databases of dynamometer tests. We corroborated these data with laboratory studies of reactions of pure MTBE and of MTBE in reformulated gasoline under conditions that simulate those in the automotive engine exhaust manifold.

Both dynamometer and on-road studies indicate that RFG results in significant reductions in automotive pollutant emissions relative to conventional gasoline. Vehicle technology also has an important impact on emissions; RFG has more pronounced emissions benefits in older vehicles (Auto/Oil, 1995; 1997).

CO emissions are reduced as a result of using RFG. Dynamometer tests have shown reductions of 21 to 28% (Auto / Oil, 1995; 1997). Actual on-road emission reductions are estimated to be 11% (CARB, 1998). An on-road study found an 18% decrease in CO emissions associated with RFG (Kirchstetter et al., 1998a).

NO<sub>x</sub> emissions are reduced by RFG. The Auto/Oil study (1997) found a 7 to 16 % reduction in NO<sub>x</sub> emissions associated with RFG. Estimates of on-road NO<sub>x</sub> emission reductions range from 11% (CARB,

1998) to a 6% decrease in NO<sub>x</sub> measured in a tunnel study (Kirchstetter et al., 1998a).

VOCs in automotive exhaust are reduced from 10 to 27% by using RFG, according to both FTP tests and on-road emissions (Auto/Oil, 1997; CARB, 1998; Kirchstetter et al., 1998a). Refueling and automotive evaporative emissions are expected to decrease about 20% in proportion to the decrease in vapor pressure associated with RFG (Kirchstetter et al., 1998b).

Benzene emissions are decreased with the use of RFG. Vehicle dynamometer tests show benzene emission decreases ranging from 34 to 47% depending on vehicle technology (Auto/Oil, 1995). A tunnel study found a 52% decrease in benzene associated with the use of RFG (Kirchstetter et al., 1998b).

Total air toxics emissions are reduced by the use of RFG by 9 to 32% in dynamometer tests (Auto/Oil, 1997). On-road toxic emission reductions are estimated to be 30% (CARB, 1998).

## **2.1 AIR QUALITY BENEFITS OF MTBE AS A COMPONENT OF RFG**

It is critical to distinguish the effects associated with use of reformulated gasoline from effects associated purely with the presence of MTBE in reformulated gasoline. MTBE and other oxygenates were found to have no significant effect on exhaust emissions from advanced technology vehicles (Auto/Oil, 1995; 1997).

Automotive CO, NO<sub>x</sub> and VOC emissions are not significantly affected by including MTBE in RFG based on dynamometer tests (Auto/Oil, 1995). Automotive benzene emissions are also not significantly affected by including MTBE in RFG based on dynamometer tests (Auto/Oil, 1995).

Automotive formaldehyde emissions increase with the addition of MTBE to reformulated gasoline. Previous laboratory studies indicate that formaldehyde is an important by-product of pure MTBE combustion at elevated temperatures, such as those in the automotive engine. Formaldehyde is also an oxidation by-product of MTBE reaction at ambient temperatures, as in the case of evaporation or emissions of unburned fuel containing MTBE. Our laboratory study confirms the production of formaldehyde from both pure MTBE and CaRFG2 containing MTBE at elevated temperatures (300°C to 800°C). Engine studies indicate that an increase in formaldehyde emissions of 13% was the only statistically significant difference between CaRFG2 with MTBE and CaRFG2 without oxygenates (Auto/Oil, 1995). Similarly, Kirchstetter et al., (1998a) found a 12% increase in on-road formaldehyde emissions associated with the use of CaRFG2 containing MTBE.

Automotive MTBE emissions also increase as a result of MTBE in RFG. Previous laboratory studies and our own measurements indicate that MTBE destruction efficiency increases as a function of combustion temperature. Especially during cold engine starts, emissions of unburned MTBE from the tailpipe are likely to be quite high. Automotive MTBE emissions are about 2.5% of total exhaust hydrocarbon (HC) emissions; evaporative MTBE emissions are 8 to 10% of the total evaporative hydrocarbon emissions (CAL-EPA, 1997a). CAL-EPA estimates that 43 tons/day of MTBE were emitted in California in 1996. Kirchstetter et al., (1998a) found a six-fold increase in on-road automotive MTBE emissions associated with MTBE containing CaRFG2.

Our laboratory studies confirm conclusions of previous studies that isobutene is an important by-product of pure MTBE combustion at elevated temperatures, such as those in the automotive engine.

Methanol is also a by-product of pure MTBE combustion at elevated temperatures in previous laboratory studies and in our own study. However, we do not observe methanol production from combustion of CaRFG2 containing MTBE. This result suggests that methanol reacts quickly to form products in the presence of the other hydrocarbons in gasoline. Vehicle and on-road studies have not reported methanol in automotive exhaust.

Tert-butyl formate (TBF) is an important combustion by-product of MTBE at ambient temperatures (e.g., in the case of evaporation or emissions of unburned fuel containing MTBE). Previous laboratory studies and our own observations confirm that TBF is not a product of MTBE combustion at elevated temperatures. Vehicle and on-road studies have not reported TBF in automotive exhaust.

## **2.2 AUTOMOTIVE EMISSIONS AND AIR QUALITY**

There is strong evidence indicating that significant air quality benefits are associated with the use of reformulated gasoline. These benefits, primarily associated with reductions in exhaust and evaporative emissions of ozone precursors and air toxics, may be achieved without the use of oxygenates in RFG. The benefits from RFG are particularly effective for older vehicle technologies. Because newer vehicle technologies are designed to operate on RFG, reformulated fuel is critical for continued emissions reductions from the entire vehicle fleet. However, it is not critical that oxyfuels be used to meet air quality objectives in most areas. Despite its clear benefits, reformulated gasoline should not be viewed as a panacea for solving automotive air quality problems, but rather as one factor that can contribute to improved air quality. Achieving air quality goals will be achieved most effectively by specifying performance standards, rather than prescriptive fuel formulations, maintaining maximum flexibility for continued technological advances.

Air quality has been steadily improving in most air basins in California. Overall trends for ozone indicate a consistent decrease in the maximum annual 1-hr concentrations, in particular for the South Coast Air basin which has the most severe ozone problem. Carbon monoxide concentrations have decreased dramatically over the past two decades, such that CO non-attainment is now only a problem in three air basins in California. Air toxics concentrations, such as benzene and 1,3-butadiene have also decreased significantly in the last decade, reducing any associated cancer risk. Determining the impact of CaRFG2 on ambient concentrations is complicated by concurrent factors, including improvements in vehicle technology, motor vehicle fleet renewal, the implementation of buy-back programs for older vehicles, increasing population, varying economic activity, meteorology, etc. While there is a benefit to any reduction in air pollution levels, there is also a cost associated with these reductions. Policies have to address all the costs associated with the implementation of a particular program, such as the use of oxygenates.

## **2.3 EFFECT OF ETHANOL/GASOLINE MIXTURES ON EMISSIONS**

The effect of adding ethanol to gasoline on automotive emissions have been studied (Auto/Oil, 1991a,b). At 10% ethanol by volume (3.7% oxygen by weight) added to conventional gasoline, there are statistically significant decreases in CO (13% reduction), VOC (6% reduction), and benzene (11% reduction). Ethanol is associated with increases in exhaust emissions of NO<sub>x</sub> (5%) and acetaldehyde (159%), as well as increases in evaporative emissions. Under ambient conditions, unburned ethanol is converted to acetaldehyde and eventually to peroxyacetyl nitrate (PAN) and formaldehyde. The ambient concentrations of acetaldehyde and formaldehyde, both air toxics and known carcinogens, are expected to increase if ethanol is substituted for MTBE as the oxygenate of choice. PAN concentrations will also increase, resulting in increased eye irritation and potential vegetation damage.

## **2.4 CONCLUSIONS**

Both dynamometer and on-road studies indicate that RFG results in significant reductions in automotive pollutant emissions relative to conventional gasoline. Vehicle technology also has an important impact on emissions; RFG has more pronounced emissions benefits in older vehicles (Auto/Oil, 1995; 1997).

Automotive CO, NO<sub>x</sub> and VOC emissions are not significantly affected by including MTBE in RFG

based on dynamometer tests (Auto/Oil, 1995). Automotive benzene emissions are also not significantly affected by including MTBE in RFG based on dynamometer tests (Auto/Oil, 1995).

### **3. HUMAN HEALTH EFFECTS OF MTBE AND ETHANOL**

The following sections review available scientific information on the health effects and toxicology of MTBE as well as some of its metabolites and combustion or oxidation byproducts, including formaldehyde, tertiary butyl alcohol (TBA) and isobutene. Our findings on the following endpoints of concern are addressed below: taste and odor, acute effects and asthma, neurologic effects, developmental and reproductive effects, and genotoxicity and carcinogenesis. Since a major alternative to MTBE is ethanol, this section also briefly summarizes the available information on health effects of this oxygenate and its relevant combustion byproducts acetaldehyde and peroxyacetylnitrate (PAN). A more detailed discussion of the human health and ecological issues can be found in the Scientific Assessment on MTBE report in Volume II.

#### **3.1 TASTE AND ODOR OF MTBE-CONTAMINATED WATER**

Taste and odor is a major issue in the use of MTBE as a gasoline additive because of public concern derived from tasting contaminated water. The taste has been characterized as “objectionable”, “bitter”, “solvent-like”, and “nauseating”. There is a wide range of sensitivity to MTBE, and the threshold for taste and odor occurs as low of 2 ug/L, but studies in the literature suggest most persons would have a somewhat higher threshold. Individual variability in sensitivity to taste and odor makes it difficult to identify point thresholds for MTBE. The taste and odor thresholds for MTBE range from 2.5 ug/L to 680 ug/L and 2 ug/L to 190 ug/L, respectively. These thresholds are dependent on several factors: individual tested, whether there were multiple samples from the same individual, different populations, chlorination of the water, and temperature of the water tested (API 1994, Prah et al. 1994, Young et al. 1996, Shen et al. 1997, OFA, 1998, Dale et al. 1998). The California Department of Health Services proposed a secondary maximum contaminant level (SMCL) for MTBE of 5 ppb based on available data of the observable detection thresholds. The SMCL is not set to protect against human health effects, but rather to maintain the integrity of the aesthetic properties of drinking water and to ensure public confidence in water for drinking and cooking use.

#### **3.2 TOXICOKINETICS OF MTBE**

Toxicokinetics is the quantitative study of how a substance is taken up, distributed to internal organs, metabolized and eliminated from the body. Animal data are extensively employed due to the difficulty of obtaining measurements non-invasively on consenting human subjects. However, controlled human experiments may also be used to elucidate the toxicokinetics of a chemical substance.

Human and animal data clearly demonstrate that MTBE appears rapidly in the bloodstream upon inhalation exposure (Prah et al, 1994; Nihlen et al, 1998a; Johanson et al, 1995; Buckley et al, 1997; Miller et al, 1997). Animal studies by several routes of exposure indicate that it is distributed to liver, kidney and brain (Savolainen et al, 1995; Bioresearch, 1990a, b). Metabolism occurs in the liver, although the extent to which MTBE could be metabolized in other tissues has not been adequately investigated. The primary metabolites are TBA and formaldehyde. Blood levels of TBA continue to increase for several hours after cessation of exposure to MTBE (Nihlen et al, 1998a; Buckley et al, 1997). MTBE is cleared from the blood

of humans and animals with a half-life of about one hour. Metabolic clearance is slightly greater than exhalatory clearance. TBA's half-life is longer; up to 10 hours has been reported in human studies (Johanson et al, 1995). TBA's longer residence time in the human body makes it a candidate for use as a biomarker of exposure to MTBE. Small quantities of MTBE and TBA are found in the urine after exposure of humans or animals, and a large fraction of MTBE administered to humans has yet to be accounted for in breath or urine. In animals, the majority of urinary elimination is due to compounds formed from further metabolic processing of TBA, including alpha-hydroxyisobutyric acid and 2-methyl-1,2 propane diol (Bernauer et al., 1998; Miller et al., 1997). Small amounts of acetone have also been detected in rat urine (Bernauer et al., 1998). Preliminary data suggest these are also the major urinary products of MTBE in human urine. Further research is needed to confirm that the same metabolites produced in rats account for MTBE administered in humans.

There are many areas of uncertainty regarding the toxicokinetics of MTBE. The extent to which absorption of MTBE occurs via oral ingestion and dermal uptake have not been characterized in humans. In addition to the aforementioned potential target organs (liver, kidney and brain), animal studies raise the possibility of MTBE distributing to muscle and male gonads. From a public health standpoint, the latter issue especially warrants further investigation in animal and human studies. Also, human studies of MTBE for the treatment of gallstones suggest MTBE may concentrate in human adipose tissue (Leuschner et al, 1991). The hypothesis that this may occur under conditions of long-term, low doses has not been directly studied under either controlled experimental or field conditions. Further, one human study (based on just two subjects) suggests that up to 9% of inhaled MTBE may be retained in the mucous membranes of the lungs (Buckley et al, 1997).

Rats serve as an appropriate model for human inhalation uptake and elimination of MTBE. Human uptake is linear over the range of concentrations studied (up to 75 ppm) (Pekari et al, 1996). Uptake is linear at least up to 300 ppm in rats, levels which are unlikely to be encountered in humans (Savolainen et al, 1985). Insufficient data are available to support comparative statements on other routes of entry and on the distribution of MTBE and its metabolites to human internal organs. Similarly, animal studies have pointed to metabolites which ought to be analyzed in human urine. While there is only very limited data to address potential variability among humans in pharmacokinetic and metabolic parameters, preliminary data suggest substantial diversity in production and clearance of MTBE could occur. Quantitative insights into human variability in metabolism are only likely to come from studies of human specimens.

An issue of central importance to estimating health risks resulting from exposure to MTBE is the finding of excess lymphomas and leukemias in rats (Belpoggi et al, 1998). One of the animal toxicokinetic studies performed to date sheds light on the tissue concentrations of MTBE or its metabolites in spleen and lymphoid tissues where Belpoggi et al. (1998) observed tumors. Biodynamics (1984a) reports low but detectable levels of label in spleen and bone marrow at 0.25, 6 and 24 hours after an i.p. dose of <sup>14</sup>C-MTBE. This study did not assess the metabolites present. The distribution of label to the same tissues in which cancers have been observed lends biological plausibility to the results of Belpoggi et al (1998). However, assessing the implications for human risk will require additional research on the *in vivo* tissue-specific metabolism of MTBE and the resultant internal doses.

### **3.3 ACUTE EFFECTS OF MTBE**

Anecdotally reported acute effects of MTBE exposure included noticeable odor, headache, nausea or vomiting, burning sensation in the nose or mouth, cough, dizziness, spaciness or disorientation, or eye irritation, among other symptoms (McCoy et al. 1995; Mehlman 1998; Moolenaar et al. 1994). Because the symptoms reported are non-specific, anecdotal, and often occurred in the context of the considerable

media attention MTBE has received, interpretation of their significance has been difficult. Epidemiological studies of MTBE or MTBE/blended gasoline have not provided consistent results, and there were methodological limitations to these studies and reports. However, studies of automobile service station workers in Stamford, Connecticut, of tanker drivers, and of the heaviest exposed individuals in chamber studies suggest that individuals heavily exposed to MTBE may suffer non-specific acute symptoms (Hakkola et al. 1997; Riihimaki et al. 1998; White et al. 1995). The low odor and taste thresholds of MTBE may be a factor in the reported acute effects. There have been several chamber studies of healthy volunteers exposed to MTBE. Subjects exposed to 75 parts per million (ppm) MTBE in air developed irritation of mucous membranes and non-specific symptoms suggestive of effects on mood (Riihimaki et al. 1998). Effects on mood may be important in light of the fact that for many subjects, 75ppm is above the odor detection threshold, and presence of an unpleasant odor may have mood effects that could be of concern in occupational settings. In other studies of lower concentrations, air quality during MTBE exposure was rated as poorer (Prah et al. 1994), but there were no symptoms (Cain et al. 1996; Nihlen et al. 1998). The absence of effects at lower concentrations in chamber studies, and the absence of consistency in the results of studies of effects of ambient exposures to MTBE, would suggest that exposure to ambient concentrations of MTBE may not greatly increase symptom prevalence. The report of The National Science and Technology Council concluded: "The largely anecdotal reports of acute health symptoms among some individuals cannot be adequately explained, but also cannot be dismissed" (NSTC 1997). We agree with that conclusion. A substantial increase in ambient concentrations of irritant MTBE combustion products, particularly formaldehyde (Environmental Protection Agency 1987; IARC 1995) could result in symptoms in sensitive individuals, a population which has not been well evaluated in studies to date.

### **3.4 INCREASE IN ASTHMA DUE TO MTBE**

It is plausible that combustion products of MTBE could exacerbate or even cause asthma (Leikauf et al. 1995), but there have been no studies to date designed to address this issue. The relationship between MTBE or its combustion products and the increase in national asthma prevalence and mortality cannot be assessed based on existing studies. Reliable trends in incidence or prevalence of asthma are not readily available for comparing rates in cities where MTBE has been used to rates in cities where it is not in use, although it is possible that trends in asthma mortality could be compared. There have been no studies designed to evaluate respiratory sensitization from MTBE, and no published clinical reports were identified that document respiratory sensitization to MTBE itself. Therefore, there is little evidence at present either to implicate or to exonerate MTBE as a cause or exacerbating factor in asthma.

There is some evidence from epidemiologic studies that residential proximity to streets with heavy traffic is associated with increased prevalence or activity of asthma in children (Duhme et al. 1996; Oosterlee et al. 1996; Weiland et al., 1994; English et al. 1998). These studies provide a model which could help evaluate the role of vehicular exhaust, and of MTBE, in asthma activity. Comparisons of the effects on asthma prevalence, incidence, and activity of heavy traffic exposure in communities using MTBE and in communities not using MTBE would help distinguish the effect of vehicular exhaust from that of MTBE and its combustion products. Chamber studies in which asthma patients who believe their illness is exacerbated by MTBE are exposed to MTBE or to MTBE blended with gasoline could help verify anecdotal reports.

Since formaldehyde, a combustion byproduct of MTBE, may exacerbate and perhaps cause asthma (Imbus 1985; Nordman et al. 1985), there is a plausible mechanism for the use of MTBE in gasoline to contribute to (perhaps small) increases in asthma incidence or severity. TBA is a skin sensitizer and could also be capable of causing or exacerbating asthma in sensitive individuals.

### 3.5 NEUROTOXICITY

A few studies have indicated that MTBE has the potential for producing effects associated with CNS depression, including headache, dizziness, spaciness, nausea and disorientation. These effects appear to be reversible on cessation of exposure. Hakkola and coworkers (1997) investigated the neurobehavioral effects arising from occupational exposure to gasoline containing 10% MTBE among a group of 101 Finnish male road tanker drivers. Among tanker drivers, there was a significant increase in fatigue; drivers with longer periods of exposure to gasoline scored higher for fatigue and hostility changes compared to those with shorter exposure. Additionally, 20% of the tanker drivers reported symptoms during the work week including (in order of decreasing frequency): headache, nausea, increased salivation, dizziness and dyspnoea. This is the only known study designed specifically to measure CNS symptoms amongst occupationally exposed workers, however, in the absence of data on MTBE blood levels in these workers, it is not possible to determine the dose required to cause the effects observed.

In animals, there is evidence that MTBE at high dose may produce neurotoxic effects, including sedation. However, these effects are reversible on cessation of exposure. There is some evidence that MTBE is distributed to the central nervous system (CNS), but potential neurotoxic effects have been incompletely evaluated. Sedation could have significance in occupational settings and further neurobehavioral research would be of value. Animal studies indicate that exposure to concentrations as high as 8000 ppm can cause symptoms of acute CNS depression that are transient and reversible. There is evidence at very high doses for ataxia, loss of righting reflex, and tremors and labored breathing, but these symptoms appear to be reversible. There is a lack of animal data assessing low dose effects relevant to determining effects in humans. There is no evidence of chronic neurologic effects from exposure to MTBE, its metabolites or combustion products.

### 3.6 REPRODUCTIVE AND DEVELOPMENTAL EFFECTS OF MTBE

No human studies or case reports were located which evaluate the reproductive or developmental toxicity of MTBE. Laboratory animal experiments have shown that when exposure occurs during pregnancy at extremely high exposure levels (2500 ppm or greater for 6 hours per day throughout the gestational period) there are maternal and fetal effects (Conaway et al 1985; Bio/dynamics 1984b,c; Tyl and Neeper-Bradley 1989; Bevan et al 1997). Of the many endpoints examined, maternal toxicity was indicated by decreased weight gain during pregnancy and clinical signs such as hypoactivity and ataxia, and fetal viability and weight gain were reduced. In the mouse but not the rabbit, high MTBE exposure caused cleft palate. However, no developmental effects were detected at doses an order of magnitude lower which are believed to be 1,000 to 10,000 times greater than actual human exposures (NRC, 1996). In two breeding studies, the evidence suggested that MTBE has little potential to cause reproductive failure, especially at doses relevant to its use as a fuel additive (Neeper-Bradley 1991; Bevan et al 1997; Bio/dynamics 1984; Biles et al 1987). However, fertility studies have only been conducted in one species, the rat. There are a few recently reported investigations indicating that MTBE may function as an endocrine disruptor in rodents (Moser et al 1996, 1998; Day et al 1998). The relevance of these findings await further studies.

Epidemiological investigations of the association between formaldehyde exposure and potential reproductive toxicity have produced contradictory results. Two studies (Hemminki et al. 1982, Taskinen et al. 1984) reported an increased risk of spontaneous abortion following occupational exposures. A later study (Hemminki et al. 1985), however, showed negative results for spontaneous abortion and congenital anomalies in offspring of occupationally exposed nurses. The significance of these findings are difficult to interpret since these studies are severely limited by poor exposure assessment and/or potential bias in recall of adverse reproductive endpoints. In autopsy service workers exposed to weekly doses of 3-40 ppm formaldehyde, no increased risks for sperm abnormalities were noted (Ward et al 1984).

In animal studies, formaldehyde has been tested for teratogenicity by three different routes of administration (oral, inhalation, dermal) in four species (mouse, rat, hamster, and dog) (Marks et al 1980; Pushkina et al 1968; Saillenfait et al 1989; Martin 1990; Overman 1985; Hurni and Ohder 1973). None of the studies detected malformations. In one study, reductions in fetal body weight were observed at the highest doses; perturbations in maternal weight occurred at the two highest doses (Saillenfait et al 1989). There is no evidence from reproductive toxicity studies of formaldehyde to suggest reproductive toxicity at doses less than those overwhelmingly toxic to the parent animals (Hagino 1968; Natvig et al 1971).

No human data was found regarding the developmental toxicity of *tertiary*-butyl alcohol (TBA). However, there are rodent studies evaluating the developmental toxicity of this compound. In two strains of mice, prenatal exposure to TBA increased resorptions, but did not change malformations, variations or fetal weight (Faulkner et al. 1989). In the rat, TBA was not teratogenic, but did reduce fetal weight, cause maternal toxicity, and increase postnatal lethality (Nelson et al. 1989; Abel and Belitzke 1992). Behavioral teratogenicity, believed to result from developmental delay, was detected in the mouse when administered TBA in the diet (Daniel and Evans 1982), but was not found in the rat after inhalation exposures (Nelson et al. 1991). It is not known if the differences between these studies is attributable to species differences in neurobehavioral response or to toxicokinetics of TBA. Thus, TBA appears to induce post-natal effects at doses that do not induce teratogenicity, suggesting that MTBE should be evaluated for such endpoints.

### 3.7 CARCINOGENESIS OF MTBE

There are no human data on which an evaluation of the carcinogenicity of MTBE can be based. However, substantial evidence from studies of chronic exposure by either oral or inhalation routes demonstrate that MTBE is carcinogenic in rats and mice. Based on a thorough review of these carcinogenicity studies, supporting data on pathology and mechanisms of tumor induction, and carcinogenicity studies of MTBE's primary metabolites (TBA and formaldehyde), we conclude that MTBE is an animal carcinogen with the potential to cause cancer in humans.

Oral exposure of Sprague-Dawley rats to MTBE resulted in an increased incidence of lymphatic cancers in females; this result was statistically significant in the high dose group (Belpoggi et al 1995; Belpoggi et al., 1998). In male rats of the same study, a statistically significant increased incidence of Leydig interstitial cell tumors (LCTs) of the testes occurred in the high dose group. LCTs were also increased in a separate study of male Fisher rats exposed to MTBE by inhalation (Bird et al., 1997; Chun et al., 1992). A clear dose-response relationship for LCTs was observed, and the increased incidence was statistically significant in the intermediate and high dose groups. MTBE also induced renal tubular carcinomas and adenomas in male Fischer rats in the inhalation study. The increase in renal cancer was significant only in mid-dose males, but early mortality in the high and mid-dose groups may have decreased the sensitivity of the bioassay. No increase in tumor incidences was observed in female Fisher rats.

In CD-1 mice, inhalation exposure to MTBE increased the incidence of hepatocellular cancers in males and females at the highest concentration tested (8000 ppm) (Bird et al., 1997; Burleigh-Flayer et al., 1992). In males of this dose group, the elevation in hepatocellular carcinomas was statistically significant; in females, the increase in adenomas was statistically significant.

Formaldehyde caused lymphatic cancers in Sprague-Dawley rats exposed orally (Sofritti et al., 1998); two other bioassays of formaldehyde in Wistar rats did not find evidence of carcinogenicity after oral exposure (Til et al., 1989; Tobe et al., 1989). Inhalation studies of formaldehyde in rats indicate that most carcinogenic action occurs locally, in the nasal and respiratory passages; distal sites are not generally affected. However, breathing habits and nasal metabolism are different in rats as compared to humans, and it is not clear whether formaldehyde could affect distal tissues in humans. The potential human carcinogenicity of

formaldehyde has been studied in a number of case-control, industrial and professional cohort, and clinical studies, IARC classified formaldehyde in group 2A; probably carcinogenic in humans based on sufficient evidence in animals and limited evidence in humans (IARC, 1995).

TBA caused an increase in renal tumors in male Fischer rats, significant in the mid-dose group (Cirvello *et al.*, 1995). Among female B6C3F1 mice exposed to TBA, a significant increase in thyroid follicular cell adenoma was observed in animals receiving the highest dose. Although NTP considered TBA to be positive in the rat, NTP concluded that there was less than clear evidence for the carcinogenicity of TBA, and consequently assigned a level of some evidence. As mentioned above, TBA has generally tested negative for genotoxicity.

### **3.8 MECHANISMS OF MTBE CARCINOGENESIS AND RELEVANCE TO HUMANS**

The mechanisms by which MTBE acts to produce cancers in laboratory animals are not yet understood. The compound or compounds responsible for MTBE's carcinogenic properties have not been definitively identified, although formaldehyde and/or TBA could play a role. Genotoxicity testing of MTBE in a variety of *in vitro* and *in vivo* assays has generally produced negative results; however, MTBE was positive in two different tests, one in mouse cells and one in male rats. Of the products formed from MTBE metabolism in the body, mutagenic activity has been established only for formaldehyde.

Further research is needed before a clear understanding of how MTBE causes cancer can be reached. The importance of mechanistic research lies in part in its ability to provide a rationale for deciding to what extent the MTBE bioassay results are predictive for human cancer risk. Several investigators have questioned the human relevance of rodent cancer results.

Some of these criticisms have focused on data analysis issues. It has been suggested that the increase in incidence of lymphomas and leukemias in female Sprague-Dawley rats (Belpoggi *et al.*, 1995) would not have been significant if these categories of cancers had not been combined in the data analysis. After consideration of the literature on pathology of lymphohematopoietic cancers in rats, and review of an updated report containing more detailed pathology data from the study authors (Belpoggi *et al.*, 1998), we conclude that the combined incidence category used by the study authors is a valid and correct measure for analysis of their experimental results. It has also been pointed out that if the incidence of LCTs in control Fischer rats in the MTBE inhalation bioassay had been closer to the historical average, rather than at the low end of the historical range, the number of LCTs observed in MTBE-treated rats would not have been increased relative to controls (Bird *et al.*, 1997). We consider the use of concurrent experimental control data for statistical analysis to be good practice. The clear dose-response curve (increase in incidence with each incremental increase in dose) for LCTs in the Fischer rat study, and the fact that LCTs were increased in two strains of rats, using different routes of exposure, further underscore the significance of the results.

The second category of concern about the relevance of the MTBE-induced rodent cancers is related to the possible contribution of species-specific mechanisms to production of LCTs and renal tubular cancers in male rats. Some mechanisms of induction of LCTs are not likely to occur in humans due to interspecies differences between rats and humans in the endocrine regulation of these cells. However, MTBE is not known to induce LCTs via any of the species-specific mechanisms that have been identified. Preliminary data from rat studies suggests that MTBE does not increase luteinizing hormone levels; most non-genotoxic mechanisms of LCT induction in rats identified to date involve elevations in luteinizing hormone. Until the mechanisms of action of MTBE and its metabolites in testicular cell biology are understood, a potential risk to humans suggested by rat LCTs should not be ruled out.

A substantial literature addresses the hypothesis that the renal tubular tumors induced by MTBE in

male Fischer rats are due to an interaction with a protein called  $\alpha_{2u}$ -globulin; this mechanism is thought to be active only in male rats and not relevant to humans. Specific criteria have recently been developed by the United States Environmental Protection Agency and the International Agency for Research on Cancer to determine whether kidney tumors observed in a particular bioassay were caused exclusively by a mechanism dependent upon  $\alpha_{2u}$ -globulin (US EPA, 1991; IARC, 1998). The data currently available on MTBE fulfill some, but not all, of the IARC and US EPA criteria. Therefore, while  $\alpha_{2u}$ -globulin may contribute to renal carcinogenesis induced by MTBE, it appears that other mechanisms are also involved. It is prudent to consider the renal tubular tumors observed in male rats indicative of potential carcinogenic risk to humans.

In conclusion, the mechanisms that have been proposed to explain the carcinogenic properties of MTBE are not adequately supported by currently available data. Unless all four of the cancer types reported in mice and rats exposed orally or by inhalation are shown to have negligible predictive value for humans, it must be assumed that MTBE poses some human cancer risk. It should be noted, however, that scientific understanding of the mechanisms by which MTBE causes cancer in laboratory animals is nascent, and therefore uncertainties remain about the nature and extent of risk for humans, especially for exposure to doses lower than those used in animal studies. Our conclusion that MTBE is an animal carcinogen and with the potential to cause cancer in humans is supported by several other comprehensive reviews of the science. A report of the White House National Science and Technology Council concluded that there is "sufficient evidence that MTBE is an animal carcinogen" (NSTC, 1997, p. 4-26) and that the "weight-of-evidence supports regarding MTBE as having a carcinogenic hazard potential for humans" (NSTC, 1997, p. 4-26). In 1997, the US EPA developed a drinking water advisory for MTBE, which states "the weight of the evidence indicates that MTBE is an animal carcinogen and the chemical poses a carcinogenic potential to humans" (US EPA, 1997a). The California Environmental Protection Agency has recently proposed that MTBE in drinking water be limited to 14 ppb to protect the California population against the risk of excess cancers arising from ingestion of MTBE (OEHHA, 1998). The methodology used in this risk assessment appears appropriate, but we expect refinements as more information on mechanism becomes available.

### **3.9 HEALTH EFFECTS OF MTBE BYPRODUCTS**

Primary metabolism of MTBE produces formaldehyde and tertiary butyl alcohol (TBA). Oxidation of MTBE in water treatment systems produces tertiary butyl formate (TBF), which then transforms to TBA, as well as formaldehyde. Combustion of MTBE results in increases in formaldehyde and isobutene emissions.

Available data for formaldehyde and TBA on asthma, reproductive and developmental effects, and carcinogenicity were addressed above, in the context of our findings for MTBE. Other relevant data are summarized in this section.

Formaldehyde produced as a combustion by-product of MTBE is absorbed by the inhalation route. Little internal exposure to formaldehyde is believed to occur because it is transformed rapidly. Animal inhalation studies fail to show increased blood concentrations of formaldehyde, probably due to local metabolism occurring in the nasal mucosa. The respiratory tract is the principal target organ of formaldehyde. Formaldehyde has been reported to cause nausea and headaches and at concentrations as low as 30 parts per billion, causes irritation of eyes, mucus membranes and the respiratory tract. There is limited evidence that formaldehyde may contribute to respiratory sensitization. Formaldehyde is a well documented skin sensitizer, and there is evidence that exposure to formaldehyde may cause or exacerbate asthma.

Since MTBE is widely distributed in the body, tissues with the capacity to metabolize MTBE to formaldehyde might be exposed to this genotoxic agent. Further studies are warranted on the generation of formaldehyde by internal organs where MTBE has been detected, such as kidney, brain, gonads, and adipose

tissue and other tissues in which important health endpoints have been observed. Potential metabolic production of formaldehyde in the spleen and other lymphoid organs merits investigation in light of lymphomas found in female rats.

Isobutene is generated as a major combustion by-product of MTBE. There is no human data on the reproductive or developmental toxicity of isobutene. Animal studies indicate decreased sperm motility in both rats and mice exposed to 8000 ppm, 6 hours per day for 14 weeks. The meaning of these isolated effects on sperm motility is unknown, however they would not be sufficient to affect fertility. There were no other effects on reproductive organs noted. There are no animal or human developmental toxicity data on isobutene. Isobutene can be transformed to a mutagenic epoxide. There is some evidence that isobutene has carcinogenic activity in male rats; carcinogenicity studies in mice were negative.

### **3.10 HEALTH CONSIDERATIONS FOR ETHANOL**

Ethanol is used in many states as an oxygenate. It is also added to gasoline in other countries such as Brazil, where it is widely used. Ethanol is known to have developmental and neurotoxic effects, but the risk at the levels anticipated in the environment from its use as a fuel or additive is unclear. IARC has determined alcohol beverages are carcinogenic to humans, but whether this is significant when ethanol is used as a gasoline additive is highly uncertain.

Use of ethanol would result in increased atmospheric concentrations of acetaldehyde and peroxyacetylnitrate (PAN). Both of these compounds have potential health effects. Acetaldehyde has been listed as a Toxic Air Contaminant in California based on evidence of carcinogenicity and while PAN has not been tested for carcinogenicity, it is genotoxic and produces respiratory and eye irritation and may produce lung damage. Recent research indicates there are free radical mechanisms by which ethanol can interact with cellular macromolecules and produce DNA damage. The relationship between atmospheric ethanol and these same free radical mechanisms requires further evaluation. Further evaluation of the potential impact of ethanol, acetaldehyde, and PAN is absolutely necessary.

### **3.11 RESEARCH RECOMMENDATIONS**

Further research into the health effects of MTBE and its byproducts is needed to evaluate human health impacts in more detail. Epidemiological and controlled human exposure studies are needed to determine whether the expanded use of MTBE could be associated with an increase in asthma incidence or severity. Because of the suggestion of behavioral effects in developmental toxicology studies with TBA, and possible neurotoxicity of MTBE, behavioral endpoints could be of concern in developmental toxicity of MTBE, and should be examined in further testing. There is a need for studies to address the tissue-specific metabolism and genotoxic potential of MTBE, particularly in those tissues that have been identified as targets for animal carcinogenesis (liver, kidney, testes, and lymphatic tissue). Analysis of the spectrum of urinary products found in exposed humans would be useful not only for comparison to the rat model, but also for the information on interindividual variability such studies could provide. Preliminary evidence that MTBE may have endocrine disrupting activities must be followed up with studies that assess possible endocrine effects in target tissues such as the testes.

The potential health effects associated with formaldehyde, a metabolite and combustion product, isobutene, a primary combustion product, and tertiary butyl alcohol are matters of concern and require further evaluation. Whether interactive effects occur between MTBE, its combustion products and other components of gasoline is unresolved.

Many other documents that have reviewed the health effects of MTBE (NTSC, 1996, 1997; NRC, 1996;

HEI, 1996; U.S. EPA, 1992, ATSDR, 1996) acknowledge there are significant gaps in our understanding and recommend additional research on the health effects of MTBE. We contacted the relevant Federal Agencies to determine the scope of ongoing research on the consequences of MTBE exposure and learned there is minimal research underway at the Federal level. There is some research ongoing in California on genotoxicity and endocrine effects, but none to address the following major issues: cancer, neurologic, asthma, and acute effects, nor is there research on the health effects of substitute compounds.

It is crucial that substitutes for MTBE be further evaluated before they are widely used as substitutes for MTBE. To replace MTBE with an untested substitute would compound the current problem. The metabolites and combustion products associated with the use of other ether oxygenates such as ETBE and TAME require further investigation. Acetaldehyde and PAN are combustion products of ethanol and have potentially significant toxicity and carcinogenicity. Further toxicological evaluation of PAN is needed. Through analysis of the toxicokinetics of ethanol to determine if acetaldehyde produced by metabolism is an issue. There is a major need for exposure modeling studies to predict the airborne concentrations of acetaldehyde and PAN that would be expected if ethanol were to be used as a substitute.

The formation of other aldehydes as products of atmospheric chemistry is a matter of concern. Overall studies of atmospheric chemistry to assess products of oxygenates and gasoline are necessary.

## **4. ECOLOGICAL EFFECTS OF MTBE AND ETHANOL**

### **4.1 ECOTOXICOLOGY OF MTBE**

Increased input of MTBE into aquatic systems has led to concerns about its effects on aquatic life. Depending on time of exposure and endpoint measured, MTBE is acutely toxic to various aquatic organisms at concentrations from 44 mg/L to more than 1000 mg/L in invertebrates (Bengtson and Tarkpea, 1983; Gupta and Lin, 1995; BenKinney et al, 1997; ENSR, 1997a,b). MTBE is acutely toxic to aquatic vertebrates at concentrations from 388 mg/L to more than 3000 mg/L (BenKinney et al., 1997; Geiger et al, 1981; Veith et al., 1983; Bengtson and Tarkpea, 1983; ENSR, 1997a,b; Paulov, 1987).

The chronic No Adverse Effects Level (NOAEL) concentration for reproduction of fathead minnows is 288 mg/L, and the concentration at which half of the test organisms die (LC<sub>50</sub>) for rainbow trout is between 880-1240 mg/L. A Maximum Allowable Toxic Concentration (MATC) level of 66 mg/L was proposed as the benchmark concentration for fathead minnows (Mancini and Stubblefield, 1997; Mancini, 1997). Toxicity of MTBE to other aquatic organisms is very low. Acute toxicity tests indicate that green algae have the lowest tolerance to MTBE with an LC<sub>50</sub> of 184 mg/L (Mancini and Stubblefield, 1997). LC<sub>50</sub> for zooplankton range from 340-680 mg/L, and the chronic NOAEL for zooplankton is 200 mg/L (Mancini and Stubblefield, 1997). All of these values are quite high compared to any expected exposure. We conclude that there is low potential for adverse ecological effects from levels of MTBE currently in surface waters, which are in the 10-100 ug/L level.

Two water samples were collected from Lake Tahoe to determine the potential impact of boat activity on laboratory bioassay species. One of these samples was collected from an area with high boat activity, the second from an area with low boat activity. Both samples were tested at the UC Davis Aquatic Toxicology Laboratory. No detrimental effects were observed in any of the test species.

Studies at the UC Davis Aquatic Toxicology Laboratory showed no statistically significant developmental

defects in fish (Japanese medaka, *Oryzias latipes*) at MTBE concentrations from 10 ug/L to 700 mg/L. There was no delay in hatching due to MTBE exposure, nor was there an effect on fry viability. These negative findings suggest that developmental toxicity is not likely to occur at environmental MTBE exposure levels.

One of the concerns about the presence of MTBE in drinking water is its potential impact on mammalian reproduction. MTBE has been reported to induce testicular tumors in rats by the oral route . We evaluated the effects of acute oral MTBE exposure on testicular function of male mice using a fecal testosterone biomarker. There was no change in unstimulated and stimulated fecal testosterone at any of the MTBE treatment levels. In addition, there was no difference in endpoint serum testosterone levels between the untreated control and MTBE dosed animals. There was no change in body or testis weight among the MTBE dosed animals when compared to control. Histological evaluation revealed no difference between control and 2000 mg/kg exposed animals.

Toxicity was found in MTBE-containing water samples treated with UV/peroxide. The UV/peroxide treatment of MTBE containing water may be associated with greater toxicity to aquatic organisms than that seen by MTBE itself. Two MTBE oxidation byproducts produced during the UV/Peroxide water treatment, tertiary butyl alcohol (TBA) and tert-butyl formate (TBF) were also studied. Animals dosed with TBA and TBF were run through the same battery of tests as MTBE. No significant effects of high dose levels of TBA and TBF on male hormone levels or testicular histology were observed in mice. This is consistent with prior results from acute studies done in rats, which showed no adverse effects of MTBE treatment .

## 4.2 ECOTOXICOLOGY OF ETHANOL

A literature search was conducted on toxicity test results of ethanol in *C. dubia* and *P. promelas* (Aquire, 1998). LC<sub>50</sub> values were more than order of magnitude higher for ethanol than for MTBE. However, ethanol affects *C. dubia* reproduction at lower concentrations than MTBE, but these concentrations are far in excess of any values that might be anticipated to occur environmentally.

## 5. EXTENT OF CONTAMINATION OF DRINKING WATER SUPPLIES

The U.S. Environmental Protection Agency has set a drinking water advisory at 20-40 ug/L based on consumer acceptance. A California state drinking water interim action level of 35 ug/L has been established. However, legislation in California has required that primary and secondary drinking water standards be in place by 1999 and 1998, respectively. Currently under consideration by CAL-DHS are values of 5 ug/L for the secondary standard, based on taste and odor concerns, and 14 ug/L as a public health goal. The following section presents our findings with respect to the level of contamination in California's water resources.

### 5.1 SURFACE WATER

CAL-DHS maintains a list of surface waterbodies used as drinking water sources. These include reservoirs, lakes and rivers. Of a reported statewide total of 245 waterbodies used for drinking water, reservoirs are the most important in terms of both capacity and population served. The largest number of waterbodies are located in the San Francisco (45), Sacramento (33), Santa Rosa (27), Metropolitan Los Angeles (22), and San Bernardino (21) regions. The capacity of these waterbodies is in excess of 60 million acre-feet of usable water, which supplies a population of more than 25 million residents with all or part of their drinking

water. The Metropolitan LA and San Francisco regions contain the majority of the total population served.

Water quality sampling for MTBE in California and nationally is relatively recent, with most monitoring programs in existence only since 1996-97. MTBE monitoring has largely been voluntary over this period and consequently not all waterbodies have been equally sampled. MTBE monitoring data is not centralized. Therefore, an extensive effort was made to contact the parties responsible for water quality or water supply for each individual source. We found that the DHS web page for MTBE in public drinking water systems (<http://www.dhs.cahwnet.gov/PS/ddwem/chemicals/MTBE/mtbesummary.htm>) did not adequately reflect the available database for California's surface waters. Of the 245 identified waterbodies used for drinking water, we were able to obtain data for 105 (43%); no MTBE measurements were made at 35 (14%) of these waterbodies, we received no response for 91 (37%), and for 14 (6%) of the waterbodies our survey shows MTBE was sampled but no data was supplied. The most complete monitoring (relative number of waterbodies sampled) was done in the Santa Barbara, San Francisco, Monterey, Stockton, Metropolitan and San Diego regions.

A striking feature of MTBE monitoring statewide was the large difference in sampling frequency between waterbodies. Sampling frequency ranged from a single sample to greater than 500 samples. Our understanding of the environmental fate and transport, and sources of MTBE is primarily based on those water bodies which were monitored extensively. Statewide, monitoring at 79, or 75% of the 105 waterbodies with data consisted of 10 or less total samples. Over 60% of the waterbodies reporting MTBE had 5 or fewer individual samples. Far fewer waterbodies were sampled in larger numbers. Between 11-50 samples were taken at 14 waterbodies, 51-100 samples at 4 waterbodies, 101-150 samples at 1 waterbody, and more than 150 individual samples were taken only at 7 waterbodies. These included Lake Perris (528), Donner Lake (363), Lake Castaic (296), Lake Tahoe (206), Lake Skinner (191), Silverwood Lake (192) and Lake Havasu (156). Of the 105 waterbodies, 39 were sampled at multiple locations and 64 were sampled on more than one date. Other waterbodies that were monitored more routinely include; Lake Casitas (112), Lake Matthews (78), Lake De Valle (73), Anderson Reservoir (62), Lake Cachuma (54), Pyramid Lake (48), Lake Oroville (48), Lake Merced (48), Lake Berryessa (38), San Luis Reservoir (36), Calero Reservoir (29), San Antonio (27), Coyote Reservoir (26), San Vicente Lake (25), Cherry Lake (24), Lake Davis (20), Modesto Reservoir (15) and El Capitan Lake (13). Because of the schedule associated with this report, the 1998 databases were not included in this analysis. The sole exception to this is Lake Tahoe which includes data from the period 1997-1998. This was done because of the special mention Lake Tahoe has in SB 521. A number of East Bay MUD waterbodies have also been extensively sampled, however, their data was not available at the time this report was written.

A total of 2,946 individual analyses for MTBE were available for incorporation into this evaluation; nearly all of these analyses were done at the 25 waterbodies listed above. The vast majority of individual MTBE analyses were either below the analytical limit of detection (952 or 32%) or if measurable, less than or equal to 5 ug/L (1,401 or 48%). Combined, approximately 80% of the total number of MTBE analyses showed a concentration less than or equal to 5 ug/L. A total of 412 analyses were in the range of greater than 5 to 14 ug/L, with 181 analyses (approximately 6%) exceeding 14 ug/L. Presented in a slightly different manner, and to avoid an undue influence of those seven waterbodies which were extensively sampled, we tabulated the number of waterbodies with at least one measured concentration in excess of the detection limit, 5 ug/L and 14 ug/L. For these conditions, 56 (53%) of the 105 waterbodies did not contain measurable quantities of MTBE. The remaining 49 (47%) waterbodies were found to have MTBE at least once. Of those waterbodies with detectable MTBE, 26 (25% of total number with data) were found to contain MTBE at levels greater than 5 ug/L at least once. A total of 13 waterbodies showed a MTBE concentration of more than 14 ug/L in at least one sample.

## 5.2 GROUNDWATER

Sources of MTBE to groundwater supplies include leaking underground fuel tanks (LUFT's), above ground storage tanks, farm tanks, leaking petroleum fuel pipelines, underground storage tanks containing fuels other than gasoline, surface spills due to automobile or tanker truck accidents, surface spills due to abandoned or parked vehicles, and precipitation. Because the LUFT's are so numerous and handle such a large volume of product, they clearly pose the most serious threat to groundwater. As of June 30, 1998 there were 32,779 known sites where chemical compounds, including gasoline as well as non-gasoline products, were discharged to the environment. 16,973 of the 32,779 sites have been closed by the twenty Local Oversight Agencies, the nine Regional Water Quality Control Boards or by the State Water Resources Control Board. Closed sites are not considered to pose a hazard to public health or to the use of the groundwater resource. Sites are closed based on available information and are not required to perform any further monitoring or remediation. Of the remaining 15,806 open sites, 8,019 have contaminated groundwater via underground storage tanks. Seventy-two percent of these groundwater sites were contaminated with gasoline (5,738 of the 8,019).

In August 1998, the SWRCB reported that 52% of the active underground storage tanks have been upgraded to meet the December 22, 1998 upgrade requirements. Based on a 2.6% annual leak rate for underground storage tanks, the number of active petroleum tanks, and the percentage of tanks yet to be upgraded, we estimate that roughly 700 of the tanks that have not been upgraded will have leaked and be discovered as part of the 1998 upgrade efforts. It is further estimated based on the percentage of open groundwater sites statewide (51%) that approximately 350 of these sites will impact groundwater significantly with gasoline and other fuels. In turn, roughly 250 of these will impact groundwater with MTBE.

According to data from the State Water Resources Control Board LUSTIS database dated July, 1998, a total of 5,738 open sites (i.e., sites still being monitored) have groundwater that was contaminated by gasoline from leaking underground fuel tanks (LUFT's). Of these, 3,180 sites (55%) have detectable levels of MTBE in groundwater according to Regional Water Quality Control Board data. (Detection limits in the RWQCB data range from 0.5 to 20 ug/L.) This total does not represent *all* the groundwater MTBE sites caused by LUFT sources because not all of the sites have been monitored for MTBE. For example, in the Santa Clara Water District and in Region 4 (Los Angeles Regions), 27% and 17%, respectively, of the groundwater-impacted LUFT sites have not yet been monitored for MTBE.

Importantly, the 55% of open gasoline LUFT-groundwater sites that have detectable levels of MTBE should not be interpreted as the probability that such a site will contaminate groundwater with MTBE. This percentage represents only a partial sampling of the gasoline LUFT sites that have resulted in the contamination of groundwater by petroleum hydrocarbons *and/or* MTBE. In the cases where groundwater has been contaminated with BTEX (benzene, toluene, ethylbenzene and xylenes, common constituents of gasoline) compounds but not MTBE, the leak either occurred before MTBE was added to gasoline, or insufficient time has elapsed for the MTBE to reach monitoring wells. Based on data presented herein and on the work of Happel et al., (1998), we expect that as many as 78% of the existing gasoline LUFT sites that have impacted groundwater will lead to MTBE contamination of groundwater. Furthermore, if a LUFT site that impacts groundwater contains gasoline with MTBE, there is virtually a 100% probability that the site will result in MTBE impacts to groundwater.

MTBE concentrations detected at the sites reported by the nine Regional Water Quality Control Boards are based on current site maximums or the maximum at the site when MTBE was first detected. Using information from four Regional Water Quality Control Boards, maximum MTBE concentrations at LUFT

sites were compiled. 36% of the sites reporting MTBE analysis had concentrations less than 100 ug/L, 48% had concentrations less than 500 ug/L (including non-detects), 80% had concentrations less than 10,000 ug/L, and 4.5% had maximum concentrations greater than 100,000 ug/L. The high concentrations found at many sites are not surprising, given the high solubility of MTBE in water, the low sorption potential of MTBE, and its recalcitrance with respect to biodegradation. These groundwater concentrations will likely increase in the future, as MTBE continues to migrate from existing sources.

Data obtained through September 17, 1998 from CAL-DHS and submitted by Local Primacy Agencies were used to identify the public water systems that have been contaminated with detectable concentrations of MTBE. CAL-DHS identified 35 public drinking water wells that have reported MTBE contamination. This number of impacted wells constitutes 1.2% of all the public supply wells that were tested for MTBE and 0.3% of all public supply wells in counties where at least one well was tested. (That is, we exclude counties in which no public supply wells have been tested for MTBE.) The 35 wells constitutes 0.25% of all public water supply wells in California. As of September 17, 1998, 9.94% of the State's public water systems served by groundwater sources have been tested for MTBE and 21.47% of the public water system groundwater wells have been tested for MTBE.

We consider the 1.2% an upper-bound estimate of statewide impacts on public water supply wells since some of these wells were presumably sampled preferentially because of their proximity to known fuel sources. Accordingly, the 0.3% can be considered a lower bound for public supply wells. Applying these same percentages, we estimate that between 29 and 128 of the State's 10,931 unsampled active public supply wells have been impacted by MTBE. Thus, the total public wells that may be contaminated currently with MTBE is estimated to be on the order of 60 to 160.

Applying 0.3% and 1.2% to the 464,621 private wells reported in California during the 1990 United States Census leads to a crude estimate of the number of private wells that have been impacted - on the order of 1,000 to 5,000 wells. These numbers could be underestimates, as the shallower depths of private wells commonly make them more vulnerable to contamination than public wells.

### **5.3 CONCLUSION**

Contamination of wells, groundwater, and surface water has already been demonstrated. This will increase as more MTBE is introduced into the environment.

## **6. EXPOSURE ASSESSMENT**

There are three most probable exposure routes for MTBE released into the environment. These include ambient air, surface water and groundwater. Exposure to MTBE via ingestion of soil is expected to be minimal due to its low affinity for soils. In this section, we identify the sources of MTBE to air and water then discuss fate and transport in surface water and groundwater. A lake and reservoir hydrodynamic model and a stochastic groundwater model are used to further investigate these processes. As part of an analysis of human health exposure, the likelihood of exposure in an urban air environment is calculated for various scenarios, including Los Angeles/Burbank, San Francisco Bay Area, Central Valley and South Coast (Orange and San Diego Counties), and for individuals near two contaminated surface water sources (Donner and Perris Lakes), which may also utilize groundwater supplies. Various populations groups were considered, including adults, children and occupational workers who may be exposed to high levels of MTBE during

their work day. At this stage we have not evaluated the risk to individuals who participate significantly in recreational activities, and may thus be exposed to significantly different doses than the average individual. An ecological risk assessment was also evaluated for salmonids in MTBE-contaminated surface water reservoirs.

## **6.1 SOURCES, FATE AND TRANSPORT OF MTBE**

### **6.1.1 AMBIENT AIR**

MTBE can be released into the atmosphere during production, transportation, distribution and from evaporative emissions from motor vehicles. Concentrations near the source of emissions can be high, on the order of 1800 ug/m<sup>3</sup> in refueling stations (HEI, 1996). Ambient concentrations measured by CARB in the various air basins range from 1 to 20 ug/m<sup>3</sup>. There is a lack of data from indoor environments, which is important since most individuals are expected to spend 70-90% of their time indoors. For this exposure assessment, it is assumed that indoor MTBE concentrations are the same as outdoors, given that there are no indoor sources of MTBE (except from a very small amount volatilized from tap water) and no significant indoor sinks of MTBE (e.g. deposition or surface reactions).

### **6.1.2 SURFACE WATER**

#### **6.1.2.1 SOURCES OF MTBE**

The most probable sources of MTBE to surface water drinking supplies statewide include: (1) fallout associated with precipitation, (2) runoff, (3) groundwater flow, (4) direct release via spills and (5) emissions from motorized watercraft.

MTBE released to the air degrades with a half-life as short as 3 days (Smith et al., 1991). In urban settings the partitioning of MTBE to precipitation can result in concentrations as high as 2-4 ug/L (Squillace et al., 1997). This should be considered as a maximum range of values; in less populated areas concentrations will be lower. Two arguments can be made against precipitation as a significant source of MTBE to surface waters. First, the concentration of MTBE in precipitation is too low to explain the absolute values of MTBE in those waterbodies containing significant levels (i.e. greater than 5 ug/L). Under the most extreme (and unlikely) case where a waterbody is completely flushed each year and fills only with precipitation containing the maximum concentrations of MTBE, the lake concentration could only be as high as 2-4 ug/L. Clearly, even this most unrealistic of cases fails to explain the observed concentrations in waterbodies. Second, the existing data bases which are extensive enough to cover an annual period show that MTBE is most likely to occur in higher concentrations in the late spring-summer-early fall. Because this is typically a period of minimal precipitation in California (i.e. dry summers) it is improbable that precipitation is of real consequence in explaining the concentrations of MTBE found surface waterbodies.

Nationwide survey data on fuel oxygenates in urban runoff collected by the U.S. Geological Survey during the period 1991-1995 found MTBE in 41 of 592 stormwater samples (Delzer et al., 1996). While it was the seventh most frequently detected volatile organic compound found in these samples, the range of concentrations was 0.2-8.7 ug/L with a median of 1.5 ug/L. Since most of California's surface water drinking sources are typically of large capacity and/or are not located where urban runoff constitutes the majority of inflow, this source is also not likely to be of major consequence, especially in light of the low median concentration found in the USGS study. Of course this does not preclude the possibility that certain, smaller waterbodies may be influenced by MTBE in urban runoff. Studies at Donner Lake, which is located

immediately adjacent to, and receiving runoff from, Interstate 80 concluded that both highway and watershed runoff were negligible contributors to the lake's MTBE content which reached as high as 12 ug/L (Reuter et al, in press).

MTBE in groundwater can enter into surface water drinking supplies through the normal subsurface flow of groundwater into lakes, reservoirs and streams. If shallow groundwater contains elevated levels of MTBE from urban stormwater runoff as suggested by the USGS (Squillace et al., 1996) or if underground storage tanks have leaked into an aquifer, this could discharge into surface waters. At this time we were unable to find any documented evidence that this has occurred. However, the possibility that this pathway could exist in specific waterbodies can not ruled out, especially those with gas stations and/or fuel storage facilities close to the lakeshore. For example, Lake Tahoe could be a potential exception. Given that plumes of approximately 1500 feet (1/4 mile) have been identified, and that many of the existing and potential LUFT sites (gas stations) are within 500-1000 feet of the lake shore, the possibility exists that MTBE could enter Lake Tahoe from this source. Data are not available at this time to evaluate the potential magnitude but any impact would be expected to be localized near the input.

The best documented case we could discover for the impact of MTBE on surface water was from an accidental spill resulting from a ruptured pipeline which carries gasoline and other fuels across the northern Sierra Nevada for use in western Nevada. The leak was first discovered in early March 1997 adjacent to Summit Creek which is in the headwaters of Donner Lake. The discovery point was approximately 3 miles from the lake's shoreline. MTBE in the influent to the on-site surface water treatment system exceeded the 35 ug/L action limit for at least a month. Further downstream in Summit Creek concentrations were measured in the 100-200 ug/L range. Tributary monitoring by state agencies, in cooperation with other responsible parties, revealed that at the point of entry into Donner Lake, concentrations of MTBE in the inflow were in the range of 20-25 ug/L for at least one week following the discovery of the spill and initiation of monitoring. It took approximately one week for concentrations to decline to less than 5 ug/L and an additional week for levels to decline further to 1 ug/L (Levine-Fricke-Recon 1997). Extensive lake monitoring by the UC Davis - Tahoe Research Group revealed no significant impact on Donner Lake; however, if Summit Creek were a drinking water supply, distribution would have been interrupted for a period as long as or greater than one month.

Monitoring and research data from a number of independent sources all indicate that exhaust from motorized watercraft is the most significant source of MTBE to lakes and reservoirs. The first evidence comes from extensive monitoring efforts at a series of four drinking water reservoirs in Southern California (Metropolitan Water District) and two reservoirs within the East Bay Municipal Water District (EBMUD). Both the extensive MWD sampling and the EBMUD monitoring also clearly show that those waterbodies used for water skiing and personal watercraft recreation exhibited higher concentrations. The seasonal distribution of MTBE in these waterbodies also clearly show the dramatic reduction in MTBE at the conclusion of the recreational season and during the winter when watercraft use is significantly less.

A second line of evidence comes from the statewide monitoring data presented above. Categorizing the 105 waterbodies for which MTBE data was available at the time this report was being prepared, on the basis of MTBE detection and the allowed use of motorized watercraft, the data strongly support the hypothesis that the use of watercraft is an important source of MTBE to lakes and reservoirs. For the 49 waterbodies which contained MTBE at concentrations above detection, 44 or 90% allowed motorized boating. Similarly, many of those waterbodies which did not allow motorized boating also did not contain measurable levels of MTBE (41 of 56, or 73%). In the 5 waterbodies that contained MTBE at detectable concentration but which did not allow motorized boating, concentrations were low averaging approximately 1 ug/L. Of the 15 waterbodies with boating but no detectable MTBE, 13 were either sampled in the winter when boating

activity is significantly reduced, were analyzed with a high limit of detection (ppb), or were represented by a waterbody sampled only once.

There are two very recent studies that examine the level of MTBE in exhaust from a variety of watercraft engine types. Both were done during the summer of 1998 in association with the Lake Tahoe Motorized Watercraft Study. The first was an experimental investigation conducted at Lake Tahoe by Glenn Miller (University of Nevada, Reno) and Mary Fiore (Lahontan Regional Water Quality Control Board, California). This work is only recently completed and not fully analyzed; however, with the investigators permission and pending further evaluation, the following general conclusions are evident.

The amount of MTBE released per meter of distance traveled from each engine type after a single pass at operation speed (and corrected for background levels) varies with engine type:

2 stroke, carbureted out board - 15 hp	34 mg/meter
2 stroke carbureted personal watercraft - 80 hp	11 mg/meter
2 stroke, electronic fuel injected out board - 110 hp	3.2 mg/meter
2 stroke, fuel injected out board - 150 hp	2.1 mg/meter
4 stroke in board-out board - 150 hp	1.3 mg/meter

Values for the two cleanest engines have a greater degree of uncertainty because of the very low levels of MTBE released from these watercraft. When gasoline is released from normal operation of a motorboat, approximately 40% of the MTBE is retained in the water, while 60% is immediately lost to the atmosphere over the short time course of these tests (less than 1 hour).

A second study conducted by the California Air Resources Board, also as a contribution to the Lake Tahoe Motorized Watercraft Study, indicated that certain watercraft have particularly high emissions of unburned MTBE.

Collectively, these data suggest that MTBE entering lake water from the exhaust of motorized watercraft are dependent on engine type, and that technologies are available which may significantly reduce MTBE loading. The older carbureted 2-stroke engines in each of these test were shown to release much larger amounts of MTBE (and other gasoline constituents) than the fuel-injected engines or the four stroke engines. However, additional field testing using specific engines and evaluation of in-lake MTBE levels based on watercraft type is needed.

#### **6.1.2.2 MTBE LOSS FROM SURFACE WATERS**

Volatilization at the air-water boundary appears to be the primary mechanism responsible for the loss of MTBE from lakes and reservoirs. Few studies have attempted to quantify this loss; however, the studies at Donner Lake reported that at the end of the boating season, MTBE loss increased to 8.1 kg/day, in other words it took 14 days to remove 50% of the original concentration (Reuter et al., in press). This is supported by the observation that even during the summer boating season, during midweek periods when boat use dropped dramatically, the measured rate of MTBE loss from Donner Lake was similar at approximately 6.5-7.0 kg/day. While this rate of loss is dependent on a number of site-specific factors (e.g. bulk-phase concentrations, wind speed, temperature, lake hydrodynamics, etc.), the calculated 14-day half-life may be fairly applicable to describe MTBE loss from the surface waters when boat use is ended. In presenting the results of a model developed to predict volatilization of MTBE from lakes and reservoirs, Malcolm Pirnie (1998) similarly concluded that loss of MTBE from surface waters follows an exponential decay with more than 80% of the MTBE mass expected to volatilize with 2-3 weeks of cessation of MTBE discharge. Confusion regarding this issue may arise from a statement in the 1993 EPA Technical Information Review on MTBE

which stated that the volatilization half-life of MTBE in lakes could be as high as 137 days. This was specifically calculated for a depth of 50 meters. However, the MTBE research and monitoring data from California waterbodies indicate that when MTBE concentrations greater than 5-10 µg/L occur, these higher levels are typically found in the surface waters above the thermocline. Indeed, the Donner Lake and Lake Perris data clearly show that thermal stratification acts to retard MTBE transport to deeper depths. The MTBE-hydrodynamic model developed by McCord and Schladow (section 6.1.2.3) as part of this current study confirms this, but shows that MTBE can be found at lower depths during periods of deep vertical mixing and turnover, or when reservoir operations results in a unique mixing regime. Should MTBE be transported into deeper waters following lake turnover, the loss rates will be slower lower than discussed above.

### **6.1.2.3 LAKE AND RESERVOIR MODELING**

Lakes and reservoirs in temperate climates typically undergo an annual cycle. During the spring and summer, water bodies become density stratified, with warm, lighter water residing as a layer at the surface, and cool, denser water at depth. This stratification inhibits vertical mixing. Dissolved substances (such as MTBE) introduced at the surface will tend to remain in close proximity to the surface. As weather cools in fall and winter, the surface layer of the lake cools and becomes denser, leading to its deepening as it mixes with the underlying water. In most cases, this deepening of the surface layer continues until the original surface layer reaches the bottom of the lake, a process known as complete overturn.

River or pipeline inflows to a lake are constrained by the density properties of the lake. Thus, the depth at which river water will intrude into a lake will depend on the river temperature and on the ambient stratification in the lake at the time of inflow. The density stratification also impacts the removal of water from lakes and reservoirs. Water withdrawals from a reservoir frequently occur at fixed depths, where stratification is present. The stratification constrains the depth over which the removed water is drawn from, a process known as selective withdrawal. Reservoir operators often try to take advantage of this process and use it to target strata of higher quality water, or to avoid strata of undesirable water. The extent to which this is possible is governed by the existing infrastructure in a reservoir.

It is possible to model these key mixing processes, and describe the vertical state of a reservoir throughout the year and through sequences of multiple years. When such a model is coupled with an MTBE fate model, the combined model may be used to explore a range of management options. A Dynamic Lake Model (DLM) which includes MTBE processes has been constructed based on the assumption that the only losses of MTBE from a lake or reservoir is from volatilization or from withdrawal of water containing MTBE. MTBE influx has been assumed to be a function of boat use only, and has been characterized as depending on emission rates from two-stroke motors, the total number of boats using the water body, and fraction of two-stroke motors on those boats.

Three lakes were simulated: Donner Lake in Sierra Nevada, Lake Perris near Los Angeles, and Calero Reservoir near San Jose. These lakes were chosen as they represent a broad range of geographical, climatological and limnological conditions. Each lake/reservoir displays unique characteristics. Donner Lake, for example, is characterized by a strong thermal stratification that isolates the deep waters from the surface. Consequently, MTBE concentrations at depth are near zero, in agreement with measurements. Lake Perris, by contrast, displays higher concentrations at depth (5-10 µg/L) due to the mixing produced by inflow from a submerged pipeline. Calero Reservoir was thermally stratified between May and October in 1997. MTBE concentrations in the surface water ranged from 5-8 µg/L, with values of 1-2 µg/L in the deeper waters. Following turnover in October-November, the model predicted an increase in MTBE in the deeper waters as a result of the transport of MTBE from the surface waters.

The successful development of a calibrated hydrodynamic-MTBE model allows a range of management alternatives for reducing exposure to elevated MTBE concentrations to be explored.

MTBE volatilization rates are generally higher in rivers and streams than for lakes. This is due to their shallow depth, rapid vertical mixing and high turbulence intensities. The model by Pankow et al., (1996) showed that MTBE in streams typically exhibits a half-life of hours to days. The statewide survey of surface waters indicated that only a few waterbodies allowing motorized watercraft had their water intake located on a stream.

### **6.1.3 GROUNDWATER**

#### **6.1.3.1 TRANSPORT AND FATE OF MTBE IN GROUNDWATER**

Transport of MTBE in groundwater is controlled by the rate of groundwater movement, concentration and longevity of the source, and dispersion (i.e., the process whereby concentration of a dissolved chemical is reduced by dilution and the contaminant front spreads faster than the average rate of groundwater movement). Unlike petroleum hydrocarbons such as benzene, transport of MTBE does not appear to be limited appreciably due to sorption (i.e., temporary retention of the contaminant on soil and sediment particles) or biodegradation by native microorganisms. Although MTBE has been shown to degrade in biologically active soils, evidence to date suggests that MTBE is not biodegrading appreciably in groundwater. Owing to MTBE's high solubility and rather large fraction in reformulated gasoline (~11% by volume), concentrations in groundwater can be very high, up to 6,000,000  $\mu\text{g}/\text{L}$  (Zogorski et al., 1996; Happel et al., 1998).

#### **6.1.3.2 MOVEMENT IN GROUNDWATER AND POTENTIAL IMPACT ON WATER SUPPLY**

To assess potential future growth in the risks posed by MTBE in groundwater, we constructed a statistical-analytical groundwater model that accounts for the dominant transport processes and calibrated the model using benzene and MTBE plume length data from Happel et al., (1998). The model predicts future growth in MTBE plume lengths, which we use as relative measures of risk. The model accounts for three-dimensional spreading of contaminant plume concentrations as affected by groundwater flow, time, dispersion, source concentration and size, sorption, and biodegradation as well as expected statistical distributions (i.e., site-to-site variability) for each of these factors.

The model considers 5,000 to 8,000 reasonable combinations of the transport factors to generate 5,000 to 8,000 simulated plumes and successfully reproduced the statistical distribution of benzene plume lengths that were estimated for 1995-96 by Happel et al., (1998). Then, by turning off the sorption and biodegradation functions and modifying the source input concentrations and time of transport, the model reproduced the statistical distribution of MTBE plume lengths estimated by Happel et al., (1998) for 1995-96. Finally, by running the model into the future, approximate growth rates of MTBE plume lengths and, in turn, MTBE risks to groundwater were estimated.

The model simulations suggest that average plume lengths for MTBE in groundwater estimated for 1995-1996 will increase by a multiple of 3 to 4 by the year 2010 and continue increasing in the future. Thus, extrapolating on the basis of the estimated 0.3 percent and 1.2 percent (percentage of public supply wells known to be impacted by MTBE today), we estimate that the risk of public water supply wells being impacted could increase to between 1 percent and 5 percent (100 to 700 wells) by 2010. The model results suggest that larger MTBE plumes will exceed 2,000 ft in length by 2010. Indeed, information from the Tahoe Basin and elsewhere in California indicate that plumes exceeding 1,000 ft in length already exist.

Actual risks to groundwater supplies may therefore grow faster than indicated by this model.

Average modeled plume volumes (volume of groundwater >5 ug/L MTBE) range from 1 acre-foot for 1995-1996 to 10 acre-feet for 2010. Because, however, MTBE is highly recalcitrant and mobile in groundwater, the actual volumes of groundwater impacted by such plumes will be much greater. Assuming water supply wells within 2,000 feet horizontally and 200 feet vertically of the edge of an MTBE plume will potentially capture MTBE, the actual impacted volumes of groundwater due to a LUFT plume (either in 1995-1996 or 2010) are on the order of 100,000 acre ft. per plume.

## **6.2 HUMAN HEALTH EXPOSURE ANALYSIS**

### **6.2.1 URBAN AIR ENVIRONMENTS**

This exposure assessment includes exposure to indoor and outdoor ambient air, as well as exposure during refueling and while driving. Exposure to MTBE volatilized while showering was also considered, as well as the ingestion of MTBE-contaminated water (2.5 ug/L). Dermal exposure to MTBE is expected to be low in comparison to inhalation and ingestion. Based on these assumptions, estimates of maximum daily doses of MTBE in adults ranged from 2.8 ug/kg-day (Central Valley) to 5.2 ug/kg-day (San Francisco Bay Area). Although the dose during refueling is not high in absolute terms, in comparison with the dose during other activities, it is high in relative terms considering the rather small exposure time (a few minutes per week).

Daily doses of MTBE for 10 year-old children were estimated to be approximately 10 to 20 % higher than daily doses for adults in the same region. Individuals who live near gasoline service stations or who use contaminated tap water may have exposures that are 1.2 to 4 times higher than the general public.

Two groups of occupational workers were also considered. Road tanker drivers can be exposed to doses as high as 170 ug/kg-day, while service station workers are on average exposed to 100 ug/kg-day. These doses are almost two orders of magnitude greater than the dose for the majority of the population, and reflect the higher occupational risk.

The exposure assessment considers an average individual and does not take into account individual variability in breathing and drinking rates.

### **6.2.2 CONTAMINATED WATER SUPPLIES**

An analysis of the exposure of humans to MTBE from drinking contaminated water was performed and the associated risk of developing cancer as a result of the exposure was determined. Drinking water supplies were assumed to originate as both surface and groundwater. Two lakes were selected as representative surface waters that supply drinking water in the state. Lake Perris is a low elevation, coastal range reservoir that is managed for multiple uses and Donner Lake is a high elevation, Sierra Nevada lake that is also managed for multiple uses. Concentrations of MTBE in ground water were obtained from modeling plume spread from a leaky underground storage tank in a representative aquifer.

We performed a probabilistic analysis that allowed us to examine the associated uncertainty in the model and the sensitivity of the exposure to the parameters used in the analyses. Uncertainty analysis refers to a determination of the variation in exposure that results from the collective variation in model inputs. The sensitivity analysis is designed to understand how the exposure changes in response to changes in model parameters.

The exposure analyses utilized information obtained from the literature, surface water hydrodynamic

modeling, and ground water hydrologic modeling to parameterize the basic exposure model recommended by the U.S. EPA. In addition, we used some refinements to the exposure model as proposed by McKone (1987) and McKone and Bogen (1992). The EPA model assumes that the concentration of MTBE is constant over time. This assumption may not be valid for surface water or groundwater, due to fluctuations in the sources (e.g. boats in use, rate of gasoline dissolution) or fate and transport processes (e.g., precipitation, volatilization). For the deterministic analyses, we used the arithmetic mean of the concentration of MTBE in the water column during the boating season. While this allows us to estimate average exposure during the year, it does not address the effect of variation in exposure. It is unclear if the health effects resulting from exposure to a constant concentration of MTBE is the same or similar to the health effects resulting from exposure to varying concentrations of MTBE, even though the two scenarios may provide the same average concentration of MTBE in the water column. For the probabilistic analyses, we used the actual distribution of concentrations generated by the hydrodynamic modeling for the surface water bodies.

Individuals can be exposed to MTBE in drinking water by all exposure pathways. Individuals ingest water by drinking and through the use of water in cooking. Tap water used for showering, bathing, and periodic washing results in dermal exposure, and inhalation exposure can occur through the volatilization of MTBE from shower water into the rest of the house. Pathway exposure factors were calculated for all pathways using parameters obtained from several sources including Brown (1998), McKone and Bogen (1992) and the U.S. EPA exposure factors handbook (US EPA 1989). Distributions used in the probabilistic assessment were obtained McKone and Bogen (1992).

MTBE is a volatile compound, and the indoor air pathway could contribute substantially to exposure. Preliminary analyses indicated that approximately 71% of the exposure is due to inhalation of indoor air, 29% is due to ingestion, and less than 1% is due to dermal contact. The large inhalation component is a result of the high volatility of MTBE that allows a high transfer efficiency from shower water to air in the bathroom and the rest of the home. Similar results have been found for other volatile organic compounds by McKone (1987). To use these exposures as doses, it must be assumed that 100% of the ingested and inhaled MTBE is absorbed into the body and reaches the target organ(s).

The CAL-EPA draft Public Health Goal (CAL-EPA, 1998) proposes 14 ug/L as the concentration at which the increased risk of developing cancer from oral exposure is one in one million ( $1 \times 10^{-6}$ ). This concentration assumes both ingestion and inhalation exposure of MTBE originating in tap water. Based on PBPK modeling and CalTox simulations, it was estimated that the dose received from inhalation is approximately one-half of the dose from ingestion. MTBE entering the body through ingestion is assumed to be absorbed completely into the gastrointestinal tract, while 50% of the inhaled MTBE is assumed to be absorbed.

We performed two exposure scenarios using a model derived from McKone and Bogen (1992), each scenario using a different assumption for the amount of MTBE absorbed into the body through inhalation. Model I assumed that inhalation exposure results in only 50% of the dose of ingestion exposure, similar to the assumptions used in the CAL-EPA (1998) document. Model II assumed that only 50% of the inhaled MTBE is absorbed, but the relative exposures are determined based on the model derived from McKone and Bogen (1992).

Using Model I and the 14 ug/L draft Public Health Goal (PHG) MTBE concentration, we calculated the exposure as  $6.8 \times 10^{-4}$  mg/kg-d. This is the average daily exposure at which the increased risk of cancer would be  $1 \times 10^{-6}$ . Using this exposure level as the target, we then determined the concentration of MTBE in the water that would be necessary to generate that same exposure target using the assumptions of Model II.

For Model II, the concentration of MTBE in the water resulting in an average daily exposure of  $6.8 \times$

$10^{-4}$  mg/kg-d is 10.1 ug/L, approximately 30% lower than the draft PHG standard. Sensitivity analyses indicate that four factors have relatively high positive sensitivities, i.e., changes in the values of those parameters result in large changes in the average exposure. Breathing rate had the highest sensitivity (0.741) followed by shower duration (0.219), water use rate in the shower (0.176), and exposure time in the bathroom (0.152). The only negative sensitivities were associated with the ventilation rates in the home, i.e., greater ventilation rates in the home result in lower average exposure.

The results from this exposure assessment indicate that the proposed PHG may not be protective enough in terms of human health, but that the proposed Secondary Drinking Water Standard for MTBE (5 ug/L) will be adequate to achieve the commonly accepted one in a million increased cancer risk.

### 6.3 ECOLOGICAL RISK ASSESSMENT

A screening level ecological risk assessment (ERA) was performed to determine the potential risk to aquatic biota from exposure to MTBE. A screening level ERA is performed to indicate that a potential ecological problem may be present. Typically, a screening assessment includes the identification of the ecological receptors of concern, the habitats involved, the contaminants, and a basic exposure analysis including identification of the exposure pathways (Polisini et al., 1998). In addition, we used information from the literature on bioaccumulation of MTBE and data on the concentration of MTBE in the water column provided by the hydrodynamic modeling of both lakes to quantify the ecological risk for the ecological receptors. Lake Perris and Donner Lake were selected as representative of aquatic ecosystems in the state.

The ecological receptors selected for the analyses are resident salmonids in the water bodies. Data on toxicity of MTBE to rainbow trout (*Oncorhynchus mykiss*) were available allowing an analysis of the potential ecological risk.

Based on its chemical properties, it is generally assumed that MTBE does not bioaccumulate to a substantial degree in biota. Both modeling and experimental studies indicate that when MTBE is brought into the body of fish, it is rapidly excreted across the surface of the gills and through urine. Ecological risk can be quantified as a hazard quotient, which is the ratio of the expected exposure of the ecological receptor to the Toxicity Reference Value. Hazard quotient values for MTBE were much lower than 1.0, indicating very little potential for adverse ecological effects.

Comparisons of the toxic effects of some other fuel oxygenates can be made based on the limited toxicity data available and Quantitative Structure Activity Relationship information. Tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE), diisopropyl ether (DIPE), and tertiary-amyl ethyl ether (TAEE) all have somewhat lower solubilities in water and are expected to have somewhat greater toxicity to aquatic organisms. All are expected to produce between 2-6 times higher hazard quotients than MTBE. However, none of the hazard quotients are expected to exceed 1.0. Tertiary-butyl alcohol (TBA), methanol, and ethanol are expected to produce 3-15 times lower hazard quotients than MTBE.

## 7. COST OF WATER TREATMENT

MTBE's properties present challenges for conventional water treatment processes. For surface waters, the most applicable water treatment option is to pump the water and pass it through one of the water treatment processes described in this section. For groundwater and contaminated soil, the best approach is to remove the gasoline residual using Soil Vapor Extraction with above-ground treatment of the extracted vapors using either an Internal Combustion Engine, Activated Carbon or Thermal Oxidizers, pumping at the same time the contaminated water for above-ground treatment using Air stripping, Granular Activated Carbon (GAC), Advanced Oxidation Processes (AOP), Biofiltration or Hydrophobic Membranes, which are described in the following pages. In-situ treatment technologies, such as engineered biodegradation, have not yet been proven effective for the treatment of MTBE at the field scale, although these technologies may play a role in the future cleanup of these sites as the technologies mature. The costs associated with groundwater site characterization and remediation are discussed in section 8 of this report.

For this analysis, we considered the following two main scenarios: (1) high levels of MTBE contamination near the fuel tank, at concentrations ranging from 100 to 5000 ug/L, which need to be remediated to protect the aquifer if it is a potential drinking water source, but which are typically pumped at low (10 gal/min) to medium (100 gal/min) flowrates; and (2) low levels of MTBE contamination in surface waters and in the vicinity of drinking water wells, at concentrations ranging from 5 to 100 ug/L, which process large (100-1000 gal/min) water flowrates. Some cases will involve higher flowrates, which can be dealt with by multiple treatment units, or higher concentrations than 5000 ug/L, but these are extreme situations which require customized designs. The two scenarios are explored through ten different cases presented in Table 1.

**Table 1. Cases Considered for the Cost Analysis of each Technology**

	1	2	3	4	5	6	7	8	9	10
Concentration (ug/L )	100	100	100	500	1000	5000	100	500	1000	5000
Flowrate (gal/min)	1000	500	100	100	100	100	10	10	10	10

For all cases, the treatment process is designed to remove MTBE down to the 5 ug/L level based on the more restrictive proposed secondary drinking water standard (taste and odor). A 20-year life for the systems and 4% discount rate are considered. Costs are estimated at the feasibility level (-30% to +50%). Other assumptions and detailed calculations are available in the Scientific Assessment of MTBE.

## 7.1 AIR STRIPPING

Air stripping involves continuously contacting the contaminated water with a large volume of air to transfer a significant fraction of the volatile organic compounds (VOCs) to the air phase. Pollutant removal efficiency is a function of the contaminant's Henry's constant, H, as well as the design of the air stripping tower. MTBE has a relatively low H at ambient temperatures, which presents a significant challenge to effectively remove it using air stripping, requiring much taller air stripping columns than for other gasoline components such as benzene. Since air stripping only involves mass transfer from the water to the air phase, additional treatment of the exiting contaminated air stream may be required, depending on local air emissions regulations. Air treatment is typically required in ozone non-attainment areas; in other air basins, if more than 1 lb/day is emitted, air treatment is usually required.

There are several air stripping tower designs, but typically the most common and cost effective design

is the counter-current packed tower, where plastic or ceramic packing is placed randomly inside a tall column, the water is trickled from above and the air is bubbled from below, to achieve a high air-water contact area. Low-profile air strippers may also be cost-competitive for small systems (less than 100 gal/min), but have not been demonstrated for MTBE removal. Several gas phase treatment systems can be used, including high temperature (thermal) oxidation, catalytic oxidation, activated carbon, filtration through a biologically active bed (biofiltration) or oxidation using ultraviolet (UV) light and ozone.

**Advantages:** Air stripping is a proven technology, which has been applied commercially to treat MTBE-contaminated water at low and very high flowrates. It can achieve high removal efficiencies, is mechanically reliable and flexible enough to handle some variations in feed stream MTBE concentrations without a significant effect on removal efficiency. If high variations are expected, air stripping may require a post-treatment polishing step using granular activated carbon to meet effluent standards. Packed air stripping units can be designed to treat up to 1,000 gal/min, with significant economies of scale. Higher flow rates require multiple units. Several commercial vendors offer the technology and there is ample expertise in their design and operation.

**Disadvantages:** MTBE is only transferred from water to air, resulting in either air emissions or expensive air treatment. Variations in water flowrate can affect removal efficiency if the tower is operated at high MTBE removal efficiencies. Dissolved iron, calcium and magnesium in the MTBE-contaminated water will eventually deposit scales in the packing material, requiring a brief shutdown period to wash the packing with an acidic solution, or eventually replace the packing material. Biological growth in the packing may also reduce removal efficiency.

**Cost estimates:** For the ten cases studied, air stripping treatment costs range from \$0.23 to \$3.55 per 1000 gallons of water treated, without air phase treatment, and from \$0.33 to \$3.22 per 1000 gallons, with air phase treatment. Detailed costs for each case are presented in Table 2 in section 7.6. The most cost-effective air phase treatment is biofiltration at high flowrates (greater or equal to 100 gal/min) and thermal oxidation for flowrates less than 100 gal/min. At low flowrates, heat recovered from the air phase treatment to preheat the influent water can result in lower overall costs than no air treatment. These cost estimates were developed using standard air stripping design equations and capital cost estimation software.

## **7.2 GRANULAR ACTIVATED CARBON**

Granular Activated Carbon (GAC) is commonly used to adsorb VOCs from water, due to its high affinity for organic compounds. Other adsorbents are also used for water treatment, but typically their cost is significantly higher than GAC and are thus applicable only to very specific operations. Due to the high solubility of MTBE, GAC is not as effective in removing MTBE from water as it is for other gasoline components such as benzene. Laboratory tests have shown that the best GAC for MTBE treatment is coconut-shell based GAC. Once the GAC has become saturated with MTBE, the adsorption capacity can be regenerated by steam stripping or it can be replaced. Regenerated GAC has lower sorption capacity, and for a low sorbing solute such as MTBE, it is recommended to replace the carbon. To avoid the risk and expense of disposing of a hazardous waste, contaminated carbon can be sent back to the manufacturers for regeneration and sale to less-demanding applications. On site regeneration using steam is cost-effective for flowrates greater than 100 gpm. The design of a GAC system has to take into consideration a sufficiently large contact time between MTBE and GAC to allow for sorption, usually called the Empty Bed Contact Time (EBCT), which in combination with the shape of the adsorption front determines the minimum dimensions of the GAC unit. Two or more units are typically operated in series, sorbing the organics in the first unit until it becomes saturated and using the second unit to polish the effluent. Once the first unit is saturated, it is taken off-line to replace (or regenerate) the carbon, while the second unit continues to treat

the water. The units switch order after the carbon is replaced.

**Advantages:** GAC is a well-proven technology for treating water contaminated with organics. Very high removal efficiencies are achieved with proper operation. GAC is a simple technology with high mechanical reliability that can handle large variations in influent MTBE concentrations as well as variations in water flow rate. Several commercial vendors offer the technology and there is ample expertise in the design and operation of GAC units.

**Disadvantages:** Natural organic matter and other dissolved organic chemicals in the influent water have a stronger affinity for GAC than MTBE, so they will displace MTBE from the adsorption sites, reducing even further the removal efficiency and increasing the carbon use rate. An abrupt change in influent concentration of other organics (for example as the benzene plume arrives at the extraction well) can result in sudden desorption of large amounts of MTBE into the effluent; monitoring of the operation is required to reduce the risk of MTBE exposure. GAC units are commercially available in specific sizes, which limits the design options in terms of EBCT and the frequency of GAC replacement, which may not be as cost-effective as if a custom-designed unit was built. The maximum GAC vessel size is typically 20,000 lb, which means that economies of scale are not possible for flowrates above 500 gal/min.

**Cost estimates:** For the ten cases studied, GAC treatment costs range from \$0.34 to \$3.85 per 1000 gallons of water treated, for water with low organic content, and from \$0.39 to \$4.71 per 1000 gallons, for water with high organic content. These cost estimates were developed using vendor information on GAC sorption properties (GRC-22). For flowrates above 10 gal/min, on-site steam regeneration was more cost-effective than replacement of GAC.

### **7.3 ADVANCED OXIDATION PROCESSES**

Advanced Oxidation Processes (AOPs) rely on the generation of large amounts of hydroxyl radical (OH), which reacts with organics in water to oxidize them to carbon dioxide and water. Several commercial technologies exist for generating hydroxyl radicals, including ozone, ozone/hydrogen peroxide, UV/ozone, and UV/ozone/hydrogen peroxide. The dominant process in all cases is OH radical reaction with the organic contaminant. There have been some limited laboratory and bench scale studies using AOPs to eliminate MTBE from water, indicating the potential for forming intermediate products such as tert-Butyl Formate, tertiary butyl alcohol, methanol and formaldehyde, if the operating conditions are not controlled adequately. Some pilot tests have been conducted, but the results are not widely available.

The main design criteria is the kinetics rate constant, which determines the residence time in the reactor and thus the overall dimensions of the system. Ozone and/or hydrogen peroxide consumption control the operating costs. Ozone solubility also limits the maximum MTBE concentrations that can be treated. For UV assisted systems, the Electrical Energy per Order of Magnitude Reduction (EE/O) controls the design of the UV lamp system, and has a significant effect on operating costs.

Other innovative AOPs are being developed, such as ultrasonic cavitation, oxidation catalyzed by titanium dioxide, and High Energy Electron Beam.

**Advantages:** MTBE is destroyed, eliminating the need for air treatment or disposal of hazardous wastes (e.g. spent GAC). Economies of scale can make this a competitive process at higher flowrates. AOPs have been used in Europe for decades for water treatment. Use of AOPs may reduce the cost of chlorination of drinking water treated to remove MTBE.

**Disadvantages:** The formation of oxidation intermediates as well as other oxidized compounds such as bromate (which has an Maximum Contaminant Level of 10 ug/L) is a significant health concern. There is

limited experience with MTBE oxidation in pilot studies, and results have not been favorable. It is important to control ozone and hydrogen peroxide doses, as well as pH and temperature. High organic loading as well as high levels of dissolved minerals in water will reduce MTBE removal efficiency. AOPs can handle small variations in flowrate and concentration, but typically a surge tank is used if large fluctuations are expected. At low flowrates, high capital costs typically limit the applicability of this technology. Few vendors have sufficient technical expertise to implement the technology. More research is needed to determine optimal operating conditions and the limitations of this technology.

Cost estimates: For the ten cases studied, AOP costs range from \$0.29 to \$4.06 per 1000 gallons of water treated. These cost estimates were developed using vendor information for UV/hydrogen peroxide and experimental information for the ozone/hydrogen peroxide system. The ozone/hydrogen peroxide system has lower total costs than UV/hydrogen peroxide.

## **7.4 HOLLOW FIBER MEMBRANE**

An innovative application of hydrophobic hollow fiber membranes (HFM) to the removal of VOCs has been developed that makes use of the fiber's porosity and the ability of the fiber material to discriminate between water molecules and organic molecules, to selectively separate them. Contaminated water is pumped through one side of the membrane while a vacuum is applied to the other side of the fiber membrane. MTBE and other organics readily transfer through the fiber in a process called pervaporation. High MTBE removal efficiencies can be obtained with relatively short fiber lengths. The fibers are placed in a module that can process approximately 10 gal/min. To process higher flowrates, multiple modules can be connected in parallel; to achieve higher removal efficiencies, modules can be connected in series. A basic unit consists of a fiber module, a water pump and a vacuum pump, with simple instrumentation to control the main operating parameters.

A certain volume of air is contaminated, as MTBE transfers from the water to the vacuum side and air is allowed to sweep the contaminants. As with air stripping, air treatment may be required if it exceeds the 1 lb/day allowance. The same technologies can be applied to treat the contaminated air. The amount of air required is about 30% of the amount required in air stripping, significantly reducing the size of air treatment systems. The influent water can be heated to achieve higher removal efficiencies, using waste heat from the air treatment unit.

The design parameters for MTBE removal have been developed through laboratory testing, which will simplify the commercial implementation of the technology. There are several membrane vendors; the membranes are currently used to remove or add gases to liquids.

Advantages: The membrane module has a very small footprint compared to all the other technologies. High removal efficiencies can be obtained in modular steps. The technology is mechanically reliable, with few moving parts. All the components are off-the-shelf items that can readily be assembled.

Disadvantages: Limited field tests have been performed. Iron, calcium and manganese will precipitate on the fiber surface, plugging the fiber's pores. Acid backwash is effective for cleaning the fibers. The useful life of a unit has not been determined. There are limited economies of scale since multiple membrane modules must be used to treat higher flowrates. A surge tank is required if significant fluctuations in flowrate or MTBE concentration are expected, to achieve the desired removal efficiency.

Cost estimates: For the ten cases studied, HFM costs range from treatment costs range from \$0.69 to \$1.46 per 1000 gallons of water treated, without air phase treatment, and from \$1.05 to \$3.96 per 1000 gallons, with air phase treatment. The most cost-effective air phase treatment is GAC. These cost estimates

were developed using vendor information

## 7.5 BIOFILTERS

Early reports on MTBE contamination in groundwaters often stated or strongly suggested that the compound was either non-biodegradable or very recalcitrant with respect to biodegradation. However, a substantial record of biodegradation in both laboratory and full scale treatment operations has now been accumulated and the following statements can be made:

- MTBE can be degraded by a number of bacterial groups. At least a few bacterial species are able to use MTBE as a growth substrate and mineralize it to carbon dioxide and water.
- Development of MTBE degrading cultures in unacclimated systems is very slow.
- Acclimated cultures can be used to inoculate treatment systems and inoculated processes have start-up times similar to processes treating more conventional substrates.
- Successful biodegradation of MTBE has been observed in at least two field biofilter installations. One is located at the Joint Water Pollution Control Plant of the Los Angeles County Sanitation Districts and the other is operated by Environmental Resolutions, Inc. at a gasoline soil vapor extraction site in Richmond, California.
- Liquid phase biological treatment in which MTBE was mineralized has been demonstrated at laboratory scale at both Rutgers University and The University of California, Davis.

Biological treatment of water contaminated with MTBE concentrations of up to several hundred mg/L has been accomplished using mixed microbial cultures by Park and Cowan (1997) and Fan (1998). Reliable and effective biodegradation of MTBE in the air phase has been demonstrated to be possible under laboratory conditions using a pilot scale biofilter (Eweis et al., 1998). Biodegradation of MTBE has been observed to occur in a full scale biofilter operating at a gasoline soil vapor extraction site in Richmond California (Romstad et al., 1998) and in a pilot scale biofilter operating at the Los Angeles County Sanitation Districts Joint Water Pollution Control Plant in Carson, California (Eweis et al., 1997).

Sufficient data is available from the literature to design a full scale vapor phase biofilter for treatment of MTBE. Such systems can be used for treatment of air from water stripping units or for treatment of soil vapor extraction off-gas. Based on experience with vapor phase biofiltration and after considering the expected groundwater concentrations in aquifers and the required product water concentrations, a biofilm reactor was considered an appropriate method of treating water contaminated with MTBE. Laboratory studies at UC Davis indicate that for treating water contaminated with 1000 ug/L, a trickling filter bed depth of 160 cm is required to remove 99.5% of the MTBE. The flow rate investigated, 0.1 liters per minute, amounts to a hydraulic loading rate (HLR) of 0.022 meters per minute (0.07 ft/min or 0.54 gpm/ft<sup>2</sup>) which is near the standard trickling filter hydraulic loading rate (Metcalf and Eddy, 1993). The trickling filter carbon loading rate was determined to be 0.57 grams of carbon per cubic meter of filter media per hour.

Research by others determined the air phase design parameters of 16 grams of carbon per cubic meter of filter media per hour and an empty bed contact time of 1 minute (Eweis et al., 1998). A biofilter bed depth should not exceed 1 meter because of head loss considerations. This has an important impact on the surface area required for the biofilter, in particular for large liquid or air flow rates.

Advantages: Biofiltration can be a very cost-effective technology for removing pollutants from either

contaminated water or air. The pollutants are usually degraded to nontoxic compounds, mostly carbon dioxide and water. There is no disposal of hazardous wastes or transfer of pollutants to another media.

Disadvantages: Biofiltration of MTBE will require pilot testing to determine the removal efficiency with the influent water characteristics, before permitting is obtained. Large footprints may be required, which is a cost factor not included in our calculations. An acclimation period is usually required, and changes in operating conditions can temporarily affect the removal efficiency. The larger systems may require more operator attention than other treatment technologies, to reduce downtime.

Cost estimates: Since the air to water ratio is very high when stripping MTBE, the air phase concentration is low. Low air phase MTBE concentrations cause the controlling design parameter to be the empty bed contact time (EBCT). Biofilters have been constructed and operated by companies working in the field. Experienced companies were contacted and provided with design parameters specific to MTBE and asked to estimate construction and operating cost for gas-phase biofilters. Costs were estimated using information provided by companies constructing and operating biofilters. For gas-phase treatment, the costs range from \$1.47/1000 gal treated for treating the air stream from a 10 gpm air stripper, to \$0.08/1000 gal for treating the air stream from a 1000 gpm air stripper.

Since fixed film biological MTBE degradation has not been practiced in industry the cost of liquid phase biological MTBE removal was estimated by two methods to obtain low cost and high cost boundaries. The low cost boundary was determined by estimating the construction and operating cost of a trickling filter with a rotary distribution system similar to those used for secondary wastewater treatment. The high cost boundary was determined by estimating the construction and operating cost of a carbon adsorption system. For MTBE concentrations less than 1000 ug/L, the hydraulic loading rate controls the design. For MTBE concentrations of 5000 ug/L, the MTBE loading rate controlled the design. The low cost estimates are shown in Table 2.

## **7.6 CONCLUSIONS AND RECOMMENDATIONS**

Liquid-phase biofiltration is the lowest cost technology at flowrates of 100 gal/min and greater. Air stripping is the second lowest cost technology for high flowrates, if no air treatment is required. Given the nature of these feasibility cost estimates, it is recommended that specific vendor quotes be obtained for each site. Hollow fiber membranes are the lowest cost treatment for flowrates of 10 gal/min if no air treatment is required, which is typical at these low flowrates. GAC will be the most cost-effective technology for flowrates on the order of 10 gal/min if air treatment is required. AOP is in all cases more expensive than the alternative technologies, and there are sufficient uncertainties at this point with respect to byproducts of AOP to warrant further study of this technology. It has the potential of being cost-competitive at high flowrates, provided it is fully tested at the field scale.

Given that air stripping and GAC are proven technologies in the field, innovative technologies such as hollow fiber membranes, AOP and liquid biofiltration should be compared on a case-by-case basis against these treatment options.

The cost of treating MTBE-contaminated water is 40 to 80% higher than treating water contaminated only with other hydrocarbons such as benzene, for conventional technologies such as air stripping and GAC.

**Table 2. Amortized Cost, Dollars per 1000 gallonstreated**

	1	2*	3*	4*	5	6	7*	8*	9*	10*
<b>Concentration (ug/L )</b>	100	100	100	500	1000	5000	100	500	1000	5000
<b>Flowrate (gal/min)</b>	1000	500	100	100	100	100	10	10	10	10
<b>Air Stripping</b>										
MTBE (no air treatment)	0.23	0.25	0.40	0.59	0.68	0.88	1.54	2.30	2.65	3.55
MTBE (with air treatment)	0.33	0.41	0.76	0.84	0.88	0.97	2.35	2.68	2.84	3.22
<b>GAC</b>										
MTBE w/low organics	0.34	0.38	0.55	0.81	0.98	1.67	1.20	1.81	2.24	3.85
MTBE w/high organics	0.39	0.44	0.61	0.93	1.15	2.05	1.32	2.09	2.62	4.71
<b>AOP</b>										
Ozone/Hydrogen Peroxide	0.29	0.41	1.17	1.52	1.68	3.48	3.55	4.19	4.19	5.78
UV/Hydrogen Peroxide	0.62	0.65	1.30	1.35	1.40	1.83	3.15	3.20	4.01	4.06
<b>Liquid Biofiltration</b>										
MTBE	0.13	0.21	0.53	0.53	0.53	0.84	3.40	3.40	3.40	3.96
<b>Hollow Fiber Membrane</b>										
MTBE (no air treatment)	0.69	0.72	0.78	0.78	1.16	1.16	1.05	1.05	1.46	1.46
MTBE (with air treatment)	1.05	1.12	1.35	1.66	2.25	3.05	1.91	2.29	2.96	3.96

\*air treatment may not be required for this system.

N.A. = not applicable, since benzene cannot dissolve to this concentration.

## 8. COST OF GROUNDWATER REMEDIATION

While no cleanup goals have been established by the Regional Boards or the State Water Resources Control Board thus far for MTBE in groundwater, the CAL-DHS has proposed a secondary maximum contaminant level of 5 ppb based on taste and odor considerations. Regional Boards require remediation of contamination to protect the beneficial uses of groundwater. If the Regional Board has designated drinking water as a beneficial use for the affected groundwater resources, then cleanup and/or monitoring will be required until it can be shown that the remaining contamination will not pose a threat to the beneficial use of the groundwater within a reasonable period of time. Given the mobility and recalcitrance of MTBE, investigation and remediation will be required for most MTBE contaminated sites.

The costs associated with investigation and remediation are highly site specific and dependent on the location of the site, the depth to groundwater, the extent of the vertical and horizontal migration of the groundwater plume, contaminant characteristics and the subsurface geology.

Some generalized estimates for site investigation costs were obtained from industry representatives. These costs ranged from \$30,000 to \$250,000 for typical gasoline station sites, with plume lengths ranging

from 20 to 1000 feet. Some sites may have a complex hydrogeological environment or large gasoline/MTBE source zones that can result in longer or deeper plumes, increasing the costs of site investigation up to \$2.5 million. Since MTBE is more mobile and less degradable than any other gasoline component, MTBE plumes will typically be 50 to 100% more expensive to characterize than comparable plumes from conventional gasoline with no MTBE. During the investigative process sites are often prepared for remediation by placing monitoring and potential extraction wells, reducing the remediation costs.

A typical gas station contaminated site requires 24 to 60 months to remediate, if soil and water treatment are done concurrently, with an average of 36 months for remediation. These estimates are based on typical BTEX plumes or on BTEX plus MTBE plumes, where the MTBE has not migrated very far. Since MTBE plumes are bigger and getting still bigger, remediation times may be substantially larger if action is delayed. Soil treatment will be required for the site regardless of the type of gasoline used, so it is not considered as a separate item. No additional costs of soil treatment are expected for sites with MTBE relative to sites with conventional gasoline components. The typical cost of soil remediation, assuming Soil Vapor Extraction (SVE) with treatment of the extracted vapors using either an Internal Combustion Engine, Activated Carbon or Thermal Oxidizers, is on the order of \$3,000 to \$6,000 per month, per site, with an average value of \$4,500 per month per site. This considers the cost of renting the SVE equipment as well as the operating costs (labor, materials, fuel or electricity, equipment maintenance, sampling and analytical costs, administrative costs). Soil remediation is typically done in the first part of the site cleanup, with an average time of 18 months and a range from 6 to 36 months. A 20% contingency is considered in our estimates. Based on these estimates, the typical gas station site costs \$97,000 for soil treatment, with a range in costs from \$22,000 to \$260,000. Soil remediation costs are not very sensitive to whether the gasoline contained MTBE or not.

Water treatment for these gas station sites is required if there is a significant risk of human exposure. Typical pumping rates for these sites range from 10 gal/min to 100 gal/min. The rate depends on several technical and economic factors. For example, to capture an MTBE plume which has extended significantly, a higher pumping rate (in an individual well or in a number of wells) is required. However, the porosity and hydraulic conductivity of the soil and water drawdown limitations may determine the maximum flowrate allowable for a particular site. Assuming the pumping is done continuously throughout the remediation time, the total volume of water pumped may range from 10 million to 260 million gallons, with an average of 80 million gallons treated. In a pump-and-treat strategy, one can anticipate pumping a volume of groundwater that is at least 10 to 100 times larger than the volume of groundwater than is contained in the contaminated plume.

According to Happel et al. (1998), the typical LUFT site has an MTBE concentration of 200 ug/L, with a range from 5 to 10,000 ug/L. Since the treatment costs depend on the concentration as well as flowrate, the information in sections 5 and 7 is used to calculate the range of costs of water treatment per site. Including a 20% contingency, the costs would range from \$140,000 to \$240,000, with a typical value of \$190,000. The cost of a similar benzene site, treated to the 1 ug/L standard, would be approximately \$55,000 to \$180,000, with an average cost of \$110,000 for water treatment.

If MTBE groundwater plumes are allowed to migrate over a period of years or decades, remediation will become significantly more difficult and costly, owing to substantially larger plume size and diffusion into fine-grained materials that are ubiquitous within most California aquifers. Thus, the cost estimates given here assume the remediation is being performed on relatively young MTBE plumes that are discovered shortly after the leak occurred. Table 3 presents the estimated overall costs of groundwater remediation for typical gasoline sites at early stages of plume migration.

**Table 3. Total Groundwater Site Remediation**

	Gasoline with MTBE		Conventional gasoline	
	Range	Typical	Range	Typical
Site investigation	\$30,000 - 250,000	\$100,000	\$23,000-190,000	\$77,000
Soil Remediation	\$22,000 -260,000	\$97,000	\$22,000-260,000	\$97,000
Water treatment	\$140,000-240,000	\$190,000	\$55,000-180,000	\$110,000
<b>Total</b>	<b>\$190,000-750,000</b>	<b>\$390,000</b>	<b>\$100,000-630,000</b>	<b>\$280,000</b>
Annualized Cost	\$95,000-150,000	\$130,000	\$50,000-125,000	\$93,000

Not all sites will require soil remediation and groundwater treatment. Based on the report by Lawrence Livermore National Laboratory (Rice et al., 1995), 80 to 90% of conventional gasoline contaminated sites (without MTBE present) may be dealt with the natural processes of dispersion and intrinsic biodegradation, also called natural attenuation. Since these natural processes have to be monitored, there are additional costs to site investigation, which may range from \$25,000 to \$50,000 per site. Therefore, the large majority of conventional gasoline (or non-oxygenated gasoline) sites will cost around \$48,000 to \$240,00, considering natural attenuation. Sites that are close to drinking water supplies must be completely remediated. Since MTBE does not significantly biodegrade in groundwater systems, MTBE plumes will continue to extend and are more likely to impact a larger volume of groundwater and/or a drinking water well. Therefore, immediate corrective action is preferred in most cases.

Pipeline ruptures typically involve significant larger volumes of gasoline released than gas stations, since large flowrates of gasoline are being pumped through the pipeline and by the time a leak is detected a significant volume of gasoline may be released. For example, a leak in the Sierra Pacific Partners Pipeline in the Placer County region resulted in the release of at least 12,000 gallons of fuel before the leak was stopped. Although the cost items are similar, one can expect that the cost of remediating a pipeline rupture will be in the high end of our previous calculations, with a soil treatment cost of around \$250,000 and a water treatment cost of \$250,000. Other costs may be incurred in this case, where the gasoline components may affect water distribution PVC pipes, as in the case of the Placer County pipeline rupture. Including site investigation costs, a pipeline spill may cost from \$750,000 to \$1,000,000 per event.

The detection of tertiary butyl alcohol (TBA), another oxygenate, increases the cost and difficulty to remediate. TBA can occur in MTBE groundwater plumes either because it was added deliberately as an oxygenate, was introduced into the fuel as an industrial by-product, or was produced as a degradation by-product.

## **9. COST BENEFIT ANALYSIS OF MTBE AND OTHER GASOLINE ALTERNATIVES**

A Cost Benefit Analysis was conducted to evaluate the net benefit associated with using MTBE in CaRFG2, as well as alternative fuel formulations meeting the CaRFG2 requirements using ethanol or non-

oxygenated RFG. Benefit and cost categories were systematically identified, and where possible quantified. The main benefit and cost categories include:

- air quality benefits of CaRFG2, which are essentially equal for all fuel alternatives;
- health costs associated with air quality costs of using the oxygenates, due to the increased emission of aldehydes;
- health costs associated with contaminated water, which include costs of averting health damages by either water treatment or using alternative water supplies;
- direct costs paid by the consumers in the form of increased prices at the pump as well as decreased fuel efficiency due to the oxygenates;
- other costs to the economy, including monitoring costs and recreational costs.

The evaluation of the air quality benefits of reformulated gasolines meeting CaRFG2 requirements in Section 2 of this report indicates that the estimated reductions in carbon monoxide, ozone, benzene and 1,3-butadiene are similar for all three gasoline formulations. The benefits of CaRFG2 decrease with time as more vehicles in California's fleet incorporate advanced emissions controls devices.

## **9.1 AIR COSTS**

As indicated in Section 2, the use of CaRFG2 with MTBE increases the emissions of formaldehyde. However, there has not been a significant increase in formaldehyde concentrations in California's urban environments. There is a concern that use of ethanol as an oxygenate will result in increased aldehydes (mostly acetaldehyde) and PAN, as products of incomplete combustion or secondary byproducts, that may pose ambient air quality problems (NSTC, 1997). Studies have shown that adding ethanol to gasoline may increase the ambient concentrations of acetaldehyde by around 1 to 2 ppbv (Gaffney et al., 1997). The current average concentration in California urban areas is 1.3 ppbv. Cost estimates of the effects of increased aldehyde concentrations from either oxygenate are highly dependent on meteorology and atmospheric removal processes which have not been modeled for most air basins in California.

The most likely replacement of MTBE is toluene, to produce non-oxygenated CaRFG2. One immediate concern is the potential increase in toluene concentrations. Toluene can be neurotoxic at high concentrations. According to the US EPA, toluene has a Reference Concentration (RfC) in air of 0.4 mg/m<sup>3</sup> or 400 ug/m<sup>3</sup>. In California, the mean concentration in air is 8.5 ug/m<sup>3</sup>. This concentration could be tripled or quadrupled and still not be close to the RfC where adverse effects would be evident. Addition of toluene to CaRFG2 apparently would not result in significant health risk or costs. Additional low dose chronic toxicity studies must be performed in order to conduct a full assessment.

## **9.2 AGGREGATE COST OF WATER TREATMENT**

The annualized cost of treating MTBE-contaminated surface and ground waters in California is estimated to be on the order of \$340 to \$1,480 million, relative to the cost that would have incurred if conventional gasoline had been used. The major treatment cost is the cleanup of UST leaks, which is expected to cost from \$330 to \$1,400 million above the cost that would have been incurred if conventional gasoline without MTBE had been used. The groundwater remediation cost includes the legacy of older leaking USTs that stored gasoline with MTBE, which will cost from \$320 to \$1,030 million per year to remediate, relative to conventional gasoline leaks. The projected cost of future leaks of MTBE from upgraded USTs is between \$7 million and \$370 million, relative to conventional gasoline.

Based on the information in section 5.2, there are an estimated 250 active UST sites that have not been upgraded and are likely to have MTBE at levels which will impact groundwater. There are an additional 3,270 groundwater sites with detectable levels of MTBE, and it is likely that 2,100 of these sites (64%) will have MTBE concentrations greater than 100 ug/L. In addition, there are approximately 54,500 tanks used for petroleum products (including gasoline, diesel, jet fuel, fuel oil, solvents, etc.), and an estimated 75-80% of these contain gasoline, or 41,000 to 44,000 tanks. The failure rate for older tanks is around 2.7%, but the failure rate for upgraded tanks is estimated to be lower, in the range from 0.5 to 2% per year, resulting in 200 to 880 new UST failures per year.

To estimate the aggregate annualized cost of water treatment, we compare the treatment of MTBE contaminated sites versus the same number of sites if conventional gasoline had still been used. The difference is important since approximately 80% of conventional gasoline leaks are dealt with natural attenuation, whereas we estimate that only 10% of MTBE/gasoline leaks can be naturally attenuated. The cost to remediate older tanks and pending UST sites will range from \$460 million to \$1,830 million, or \$320 million to \$1,030 million more than if conventional gasoline had been used continuously. For new upgraded tanks, annualized costs will be \$38 million to \$660 million if MTBE continues to be used, or \$26 million to \$290 million more than conventional gasoline. Table 4 summarizes the calculations.

**Table 4. Aggregate Annualized Cost of UST Treatment**

	Number of USTs	Gasoline with MTBE		Conventional Gasoline	
		90% full remediation	10% natural attenuation	20% full remediation	80% natural attenuation
Older active USTs	350	M\$60-240	M\$2-11	M\$7-44	M\$13-70
Older UST sites	2100	M\$360-1,420	M\$40-160	M\$42-270	M\$81-420
Subtotal	2450	M\$420-1,660	M\$42-170	M\$49-310	M\$94-490
Annual upgraded tank failures	200-880	M\$34-590	M\$4-68	M\$4-110	M\$8-180

Pipeline failures also represent an important water treatment cost. Based on information from the Office of the California State Fire Marshall (CSFM), there are 30 to 35 leaks per year in the 7,400 miles of pipeline they monitor. There are an estimated 250,000 to 300,000 miles of pipeline in California, of which 45% are used to handle refined petroleum-based products. Assuming that 70% of the refined product is gasoline with MTBE, there are approximately 79,000 to 95,000 miles of pipeline that transport gasoline with MTBE. Many of these pipelines pass through private property and are thus not monitored by CSFM. If the failure rate is similar for the larger network, then there are an estimated 370 to 450 pipeline failures that release MTBE into the environment. A conservative estimate of the number of releases that impact groundwater would be on the order of 100 to 150 events per year, at an annualized cost of \$15 million to \$38 million. If only conventional gasoline was in use, the cost would be approximately 25 to 30% less, or \$10.5 million to \$28 million

Treatment of contaminated drinking water from surface water reservoirs is estimated to cost \$4 to \$30 million. We base our estimate on the number of reservoirs that can be contaminated based on the use of recreational boating, and an estimate of water supplied by these reservoirs. It is uncertain how many surface water reservoirs will become contaminated above the 5 ug/L level, and whether through management of the reservoir by the water suppliers can reduce or eliminate the treatment costs.

Treatment of contaminated public and private drinking water wells is estimated considering 60 to

340 contaminated public wells and 1200 to 2000 contaminated private wells. The public wells pump an estimated 3 to 90 billion gallons of water per year, with an average annualized treatment cost of \$1.8 million to \$36 million. The private wells pump an estimated 0.6 to 2 billion gallons per year, with an average annualized treatment cost of \$1.2 million to \$4 million.

The annualized cost of treating water supplies contaminated with MTBE, relative to the cost that would have been incurred if conventional gasoline with no MTBE had been used, is summarized in Table 5. Given the uncertainty in the estimates, the values are rounded to reflect at most two significant figures.

**Table 5. Aggregate Annualized Cost of Water Treatment<sup>1</sup>**

	Low Estimate	High Estimate
Older UST sites	\$320 million	\$1030 million
Future UST sites	\$7 million	\$370 million
Pipelines	\$5 million	\$10 million
Public Wells	\$2 million	\$36 million
Private Wells	\$1 million	\$4 million
Surface Water	\$4 million	\$30 million
<b>Total</b>	<b>\$340 million</b>	<b>\$1,480 million</b>

<sup>1</sup>relative to conventional gasoline

A literature review indicates that the cost of using ethanol in terms of risk to the water supplies is low. Ethanol plumes will biodegrade fairly rapidly. Undocumented studies indicate that if ethanol and BTEX are present, the intrinsic microbial population will preferentially degrade ethanol rather than BTEX, potentially extending the length of the BTEX plume. Further studies are required to determine if this is a significant concern. In the event that water supplies become contaminated with ethanol, the available toxicological information does not support treating the water to the low levels required by MTBE, and filtration in biologically active GAC would probably be a cost-effective option. We consider the incremental costs of water treatment to be negligible relative to conventional gasoline, since BTEX compounds in the gasoline fraction would determine the treatment design, rather than ethanol.

For non-oxygenated gasoline, the differential cost of remediation and/or water treatment relative to conventional gasoline is small. The increased volumetric fraction of toluene in non-oxygenated CaRFG2 will result in higher initial toluene concentrations, but toluene is easily biodegraded by the intrinsic microbial communities. It is likely that natural attenuation will be applicable at the same rates as for conventional gasoline. Above-ground treatment costs may increase at most 10% relative to treating water contaminated by conventional gasoline. Using the calculations in Table 7, this could represent an annualized cost increase of \$600,000 to \$10 million relative to conventional gasoline. This is based on the failure of 30 to 880 USTs per year, and considering that site investigation and soil remediation costs are the same as for conventional gasoline; the only difference is the incremental cost of above-ground water treatment.

### **9.3 COSTS OF ALTERNATE WATER SUPPLY**

Some utilities are faced with using an alternate water supply, at least in the short term (e.g. the city of Santa Monica). Using the figure of \$440 per acre-foot or \$1.65/1000 gallons that Santa Monica pays for water from the Metropolitan Water District as an alternative to their contaminated groundwater, we can estimate the cost of replacing 20 % of the potential 8 to 40 billion gallons of contaminated water per year if this is the amount of annual water consumed that would be contaminated by groundwater contamination and surface water contamination. The total cost per year for alternate water supply would be \$3 million to \$12 million. We assume that this is a temporary measure for most utilities, since the cost of water treatment would be lower. In addition, if many utilities took this route, the cost of alternate water would likely increase, making it much more attractive to opt for a treatment system.

### **9.4 DIRECT COSTS OF FUEL PRICE INCREASE AND DECLINE IN FUEL EFFICIENCY**

The increase in the market price of fuel due to the addition of MTBE at high levels has been estimated using weighted averages of wholesale and retail prices. The estimated annualized increased cost to the California economy is \$280 million to \$970 million, based on an estimated price increase of 2 to 7 cents per gallon of CaRFG2 with MTBE.

The decline in fuel efficiency is due to the lower energy content of MTBE with respect to other gasoline constituents, and is estimated at 1.5-3% (NSTC, 1997). This translates into an estimated cost of \$300 to 400 million per year, assuming an average cost of \$1.38 per gallon of gasoline. The combined total of the market price increase and decline in fuel efficiency is \$580 million to \$1.4 billion per year.

The California Energy Commission study provides useful information regarding ethanol demand, supply, and prices under several cases of blending concentrations (CEC, 1998). The actual percentage of ethanol in CaRFG2 can vary significantly, in particular if the refineries can obtain a waiver from CARB to use 3.5 wt% oxygen content (10 % ethanol). The range listed in Table 2 indicates the value of direct cost increase with and without a waiver. Since the waiver results in a higher ethanol content (3.5%), the cost increases due to more ethanol blended in the gasoline. Fuel efficiency also depends on the ethanol content. The decreased fuel efficiency is \$288 million per year without a waiver and \$575 million with a waiver. The combined total of the market price increase and decreased fuel efficiency for ethanol is \$500 million per year without a waiver and \$1.2 billion per year with a waiver.

In the case of non-oxygenated CaRFG2, the costs to the refinery can go from -2 to +2 cents per gallon, since toluene is currently cheaper than base gasoline. However, if all gasoline was non-oxygenated, refiners would have to purchase toluene in the open market, potentially raising the landed cost of toluene. Toluene may have to be imported from overseas to cover California's demand, resulting in higher transportation costs. Fuel efficiency is expected to increase by about 0.8 to 1.2% if non-oxygenated gasoline is used, relative to conventional gasoline, resulting in a net benefit.

### **9.5 MONITORING COSTS**

Estimates for the statewide annual monitoring costs of lakes and surface water reservoirs are drawn from recorded monitoring costs at the East Bay Municipal Utilities District reservoirs (Tikkanen, 1998). For most surface water reservoirs, these costs will be on the order of \$10,000 to \$25,000 per year, per reservoir. There are 765 surface water reservoirs used for drinking water, but based on the inventory, we estimate that those used also for recreational boating are approximately 115 reservoirs. Experience has shown that specific monitoring for MTBE is done only in those drinking water reservoirs which have recreational boating use. The frequency of monitoring groundwater sources for MTBE is expected to increase,

to protect human health. Overall, we estimate that monitoring costs will be on the order of \$2 to \$4 million per year.

Monitoring for ethanol or toluene would likely be incorporated into the periodic sampling for volatile organic compounds that public water utilities perform and report to CAL-DHS. We consider that this cost would not be significant for ethanol-based gasoline formulations or non-oxygenated gasoline, relative to conventional gasoline.

## **9.6 RECREATIONAL COSTS**

Foregone boating expenses (entrance fees, gasoline, distance traveled) are summed using data from several reservoirs. Reservoirs were classified by boating facilities (major, equipped and usual) and reservoir size (small, medium and large). The aggregate travel cost is estimated at \$160 to \$200 million. We consider that all 115 dual use reservoirs will eventually implement some restrictions to maintain their MTBE levels under control. Depending on the severity of MTBE contamination, restrictions may range from 20 to 100% of boating activities in these reservoirs.

Based on our preliminary estimate of the risk of using ethanol-based CaRFG2 or non-oxygenated gasoline, these formulations would probably not result in the need for boating restrictions for water-supply reservoirs. However, as we indicate in the next section, all gasolines contain many chemicals which are not desirable in our drinking water or that can have ecological damages, however small. Setting emissions standards for motorized watercraft, and inspection programs to enforce them, will have a positive impact on all multi-use reservoirs, regardless of the gasoline formulation.

## **9.7 EFFECT OF MTBE ON VEHICLE PARTS**

Based upon a literature review that consists of technical reports, service manual guidance and articles appearing in the automotive engineering field, it can be concluded that MTBE-containing gasoline does not affect the performance or the longevity of the vehicle. The effects of MTBE-containing gasoline on a number of vehicle components are nearly the same when compared to using the same base fuel. When using gasoline containing MTBE, the rubber hosing in older vehicles may need to be replaced with more compatible elastomers. Ethanol-containing gasoline may lead to increased “knock” under certain conditions that may require changes to engine timing or fuel flow rate. Fuel tank barrier technology improvements can compensate for the use of alcohol and oxygenated fuels. The use of RFG, oxygenated or non-oxygenated, is not expected to increase the normal cost of motor vehicles or their operation, except for the decrease in fuel efficiency which we considered before.

## **9.8 EFFECT OF MTBE ON UST MATERIALS**

The review of the available literature indicates that no significant threat exists to UST materials from MTBE-containing fuels as long as the concentration of MTBE is less than 20% by volume. The most vulnerable materials in UST systems are elastomeric sealing components, some of which have exhibited significant amounts of swelling when in contact with 15% to 20% MTBE-containing fuels. Although deemed significant, the amount of swell associated with these concentrations did not adversely affect the ability of the material to perform its required function. Fiberglass materials exhibit no significant volume changes when in contact with MTBE-containing fuels (Sun, 1998); and one manufacturer of fiberglass USTs reported very little effect on the laminate used in their tanks (Davidson, 1997). Furthermore, at least

one fiberglass tank manufacturer has warranted the use of their tanks for 30 years with fuels containing up to 20% MTBE (Davidson, 1997). No evidence of any permeability testing for fiberglass UST components was found in the literature, however. Metallic UST components have not been shown to exhibit significant changes in physical properties stemming from exposure to MTBE-containing fuels in liquid phase. These studies indicate that no significant threat exists to UST systems from the concentrations of MTBE likely to be present in reformulated fuels (Alexander, Ferber, Stahl, 1994; Aloisio, 1994; Sun Refining and Marketing, 1998).

## **9.9 CONCLUSIONS OF THE COST BENEFIT ANALYSIS**

Based on the analysis of the major costs and benefits associated with the three gasoline formulations, we conclude that non-oxygenated CaRFG2 achieves air quality objectives at the least cost, followed by CaRFG2 with ethanol. The water treatment costs associated with CaRFG2 with MTBE make this the most expensive gasoline formulation, when all costs are considered. Other important costs include the direct price increase paid by consumers for oxygenated gasolines, and the potential loss of recreational boating activities if MTBE continues to contaminate surface water reservoirs. There are several policy options that can reduce the economic impact of using MTBE, or that can achieve air quality benefits at a lower cost.

## **10. ECONOMIC EVALUATION OF POLICY OPTIONS**

In addition to the major choices in the types of fuels (i.e. MTBE, ethanol) which can either be implemented through regulation or through relaxation of gasoline performance requirements (e.g. Reid Vapor Pressure), there are many policies that can be implemented to reduce the costs while maximizing the benefit. For example:

- 1) Restrict the use of CaRFG2 with oxygenates to Federal non-attainment areas.

CARB has redesignated Los Angeles, Orange, Riverside, Ventura, San Bernardino, Imperial, San Diego and Sacramento Counties as non-attainment areas for air pollutants. These counties still represent a significant fraction (> 70%) of the gasoline market. The cost benefit analysis indicates that non-oxygenated CaRFG2 has clearly a higher benefit/cost ratio. All areas in attainment should phase out oxygenated gasoline in the next few years, and non-attainment areas should use non-oxygenated CaRFG2 during the rest of the year. The length of the summer and winter seasons for each non-attainment area should be reviewed to minimize the use of oxygenated gasoline. California should actively promote the passage of HR Bill 630 and Senate Bill 1576 to eliminate the oxygen content requirement, which is not only not cost-effective in terms of emissions reductions, but also raises many issues in terms of water resources.

- 2) Internalize the cost of MTBE-contaminated water treatment through a surcharge on underground storage tanks and gasoline.

This policy is suggested in order to extend the existing Underground Storage Tank Cleanup Fund Program (USTCF) beyond the year 2005 when tank owners are scheduled to stop paying an annual fee as part of the financial responsibility compliance requirements through 40 CFR 280. If the \$0.012 per gallon fee per tank is maintained, the fund would continue to generate \$90 million annually. Given the expected increase in claims from USTs that stored gasoline with MTBE, the fund will most likely need to be extended

and increased. With the requirement that tanks be upgraded to new, safer standards by the end of 1998, the probability of claims should begin to decrease over time, but it will probably take several years to complete the backlog in sites to be remediated.

3) Promote vehicle retirement programs and new vehicles to achieve air emissions reductions.

Accelerated vehicle retirement programs have been implemented in four air basins within the state with significant success in terms of reducing air emissions (reactive organic gases, carbon monoxide, nitrous oxide and sulfur dioxide) that increase with vehicle age. The programs can be expanded to other areas to achieve reductions above and beyond what can be achieved by fuel changes. A feasible target for vehicle retirement is 40% (or 40,000 per year) of the vehicles on the road that do not have catalytic converters, over the next 10 years. The emissions reductions would be significant in all four pollutant categories identified above. The total cost is \$15 - \$24 million per year over the next 10 years based on a range of \$500-\$800 per vehicle. An increase of \$1 in the vehicle registration fee statewide could finance the program. The removal of emissions through this program is much more cost-effective than using oxygenated CaRFG2 without placing water resources at risk.

4) Management of surface water reservoirs to reduce levels of contamination.

Santa Clara Water Agency has gained significant experience recently in implementing Best Management Practices and restrictions on surface water reservoirs that can serve as a useful model for the management of surface reservoirs around the state. Best Management Practices have little cost to the water district or the consumers. Programs that incorporate restrictions consisting of limited permits for a designated number of motorized watercraft and/or temporary bans on all motorized watercraft can be used in conjunction with water quality monitoring to ensure MTBE levels in the reservoir are below the secondary MCL. Boating restrictions should be considered in conjunction with incentives to change to new engines that meet strict emissions standards. As with automobile smog checks, routine emission inspections of motorized watercraft should be mandatory to ensure that high emitters are removed from the fleet.

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