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FEB 16 1999

February 11, 1999

Dr. C. W. Jameson
National Toxicology Program, Report on Carcinogens
79 Alexander Drive, Room 3217
P.O. Box 12233
Research Triangle Park, North Carolina 27709

Dear Dr. Jameson:

The California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA) considers the National Toxicology Program (NTP) to be one of the world's leading scientific organizations with respect to the testing and evaluation of chemicals for carcinogenicity. Moreover, the NTP's Report on Carcinogens (RoC) is widely regarded as an authoritative source of information on chemical carcinogens. OEHHA appreciates this opportunity to provide comment on NTP's recently proposed additions and deletions to the Ninth Report on Carcinogens. OEHHA has some concerns related to the implementation of the external peer review process (i.e., the Board of Scientific Counselors RoC Subcommittee) in which chemicals are considered for addition or removal from the RoC. In addition, we are providing comments on diesel exhaust particulates, nickel compounds, ethylene oxide, ethyl acrylate, and methyl tertiary butyl ether (MTBE).

It appears to OEHHA that under the current process the RoC Subcommittee is provided with less than adequate time at their meetings to conduct the in-depth discussions necessary for thorough consideration and deliberation on agents with complex toxicological data sets. It is unclear to us whether the RoC Subcommittee has had adequate opportunity to fully review the original data and other background materials, prior to their meetings. Without such opportunity, they may have been forced to place undue reliance on secondary sources, including reports prepared by subcontractors, and petitions submitted by interested parties. In evaluating the carcinogenicity of agents for which the evidence is complex, the RoC Subcommittee should give primary consideration to original data published in the peer-reviewed scientific literature or submitted according to regulatory guidelines. OEHHA suggests that NTP ensure availability of all necessary original data to the RoC Subcommittee, and where appropriate provide evaluations by NTP's own highly knowledgeable and respected staff, rather than relying on subcontractors or interested parties to provide briefing materials. Also, in order to foster public confidence in the

process, NTP should post the background materials used by the RoC Subcommittee to evaluate each chemical on its Web site.

OEHHA supports the use of mechanistic data in reaching decisions on listings in the RoC, but notes the need for caution and careful evaluation of data in applying this type of information. It is particularly important that mechanistic hypotheses be adequately tested prior to their acceptance and use in hazard identification. All plausible hypotheses, including the null hypothesis, need adequate consideration and exploration of their implications for hazard identification. This may not always be possible, due to the tendency for certain hypotheses to be espoused by energetic protagonists, while other equally valid possibilities receive less than their due consideration. We encourage NTP, as an objective institution, to step in where necessary to develop additional experimental information to test mechanistic hypotheses.

OEHHA supports the decision to list of diesel exhaust particulates as "reasonably anticipated to be a human carcinogen". In 1998, the OEHHA and the Air Resources Board completed a comprehensive risk assessment document on diesel exhaust particulates, entitled "*Proposed Identification of Diesel Exhaust as a Toxic Air Contaminant.*" This enclosed document considers the available scientific evidence as to the health effects of diesel exhaust particulates, and includes a thorough review and analysis of the extensive literature concerning the carcinogenic potential of diesel exhaust. Pursuant to the California regulatory framework, this document was developed via an open, public process with much opportunity for public comment and response as well as independent scientific peer review. The document found that the epidemiological evidence was consistent with a causal relationship between occupational diesel exhaust exposure and lung cancer.

OEHHA supports the decision to upgrade the listing of nickel compounds to "known to be a human carcinogen". Our enclosed document, "Proposed Identification of Nickel as a Toxic Air Contaminant" presents a comprehensive 1991 cancer risk assessment of nickel compounds, including soluble nickel. This document was also developed via an open, public process with much opportunity for public comment and response as well as independent scientific peer review.

OEHHA supports the decision to upgrade the listing of ethylene oxide to "known to be a human carcinogen". We are very much encouraged to see mechanistic and genotoxicity information used by the RoC Subcommittee to support the interpretation of the substantial, but complex, body of evidence for the human and animal carcinogenicity of ethylene oxide.

We would like to comment on the RoC Subcommittee's recommendation to remove the listing of ethyl acrylate as "reasonably anticipated to be a human carcinogen". The decision appears to be based on an untested hypothesis regarding level of risk, rather than hazard

identification. That is, while ethyl acrylate is a reactive molecule with a proven ability to generate genetic damage of the clastogenic type, there is rapid metabolism to inactive products under most conditions *in vivo*. Consequently, the hypothesis is that ethyl acrylate exposure is likely to cause clastogenicity and/or carcinogenesis only at the site of high chemical exposure and humans are not likely to encounter such conditions. It appears that consideration of the likelihood of human exposure to high levels of ethyl acrylate played a significant role in the RoC Subcommittee's decision. In the risk assessment of carcinogens, the hazard identification stage should clearly identify any material capable of causing, or reasonably expected to cause cancer in humans by any route. As shown by NTP (1986), and endorsed by the IARC (1986) evaluation, ethyl acrylate meets this criterion. The likelihood of this outcome under a given set of circumstances with regard to route, level and duration or frequency of exposure is the proper concern of a later stage of the risk assessment process. It is undesirable to confuse these separate stages since this could unjustifiably shield from consideration some other exposure scenario, not presently foreseen, where a significant risk would be predicted by these same considerations and models. Particular caution should be used in the case of ethyl acrylate, where there is an unexplained epidemiological association with colon cancer. Although this latter finding is hard to reconcile with other experimental evidence, it remains possible that future experimental studies or workplace observations will reconcile all these different results. The interpretation of epidemiological studies needs to consider both the power (or lack thereof) of negative findings to exclude certain conclusions, and the confidence which may be placed in any apparent positive associations.

Finally, we wish to comment on the RoC Subcommittee action not to recommend listing MTBE as "reasonably anticipated to be a human carcinogen". We are providing further information on this agent, and wish to request a re-evaluation of MTBE for the 9th or 10th RoC, since the issues raised concerning this agent's carcinogenicity are difficult and need to be looked at in greater depth. At the time of the re-evaluation, new data, including any new analyses, should be considered. This re-review should also consider the toxicological information on the metabolites of MTBE.

The available toxicological data on MTBE have undergone several extensive reviews, analyses, and evaluations this past year in California, as a result of two separate laws enacted by the state legislature during 1997. One comprehensive review was conducted by the University of California; several other reviews were conducted by OEHHA. In each report that evaluated the evidence of carcinogenicity of MTBE, a conclusion was reached that MTBE is an animal carcinogen with the potential to cause cancer in humans. The purpose, scope, and conclusion of each of these recent California health-based evaluations of MTBE are briefly discussed below.

The MTBE Public Health and Environmental Protection Act of 1997 directed the University of California to conduct an assessment of the health and environmental effects of

MTBE. Volume II of this November 1998 *Health and Environmental Assessment of MTBE. Report to the Governor and Legislature of the State of California as Sponsored by SB 521*, contains an exhaustive evaluation of the health effects of MTBE. This evaluation includes a thoughtful and extremely thorough evaluation of the evidence relevant to carcinogenicity and carefully examines the various criticisms and issues raised regarding the completeness and appropriateness of the reporting and analysis of the bioassay data, and the relevance of the observed tumor sites to human cancer risk. The report states "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". We are enclosing Volume II: *An Evaluation of the Scientific Peer-Reviewed Research and Literature on the Human Health Effects of MTBE, its Metabolites, Combustion Products and Substitute Compounds*, for your consideration.

The Local Drinking Water Protection Act of 1997 directed the California Department of Health Services to develop a primary maximum contaminant level (MCL) that addresses health concerns, by July 1, 1999. In accordance with California procedures for development of such primary MCLs, DHS requested OEHHA to conduct a risk assessment on MTBE. In the meantime, the California Safe Drinking Water Act of 1996 requires OEHHA to adopt Public Health Goals (PHGs) for contaminants in drinking water based exclusively on public health considerations. Therefore, OEHHA developed a document entitled "*Public Health Goal for MTBE in drinking water*", which included the derivation of a numeric PHG for levels of MTBE in drinking water based on carcinogenic effects observed in experimental animals. In evaluating the evidence relevant to carcinogenicity, this assessment addressed the appropriateness of the reporting and analysis of the bioassay data and the relevance of the observed tumor sites to human cancer risk. The document states: "As a result of this assessment OEHHA considers MTBE to be an animal carcinogen and a possible human carcinogen". We are submitting the June 1998 draft of this document, *Public Health Goal for Methyl Tertiary Butyl Ether (MTBE) in Drinking Water*, for your consideration. The final draft should be completed by the end of this month.

The Local Drinking Water Protection Act of 1997 also required the State's qualified experts (i.e., the Carcinogen Identification Committee and the Developmental and Reproductive Toxicants Identification Committee) for the Safe Drinking Water and Toxic Enforcement Act of 1986, also known as Proposition 65, to make a finding on or before January 1, 1999 as to whether MTBE has been clearly shown through scientifically valid testing according to generally accepted principles to cause cancer or reproductive toxicity. In support of this requirement, OEHHA developed documents evaluating the evidence on the carcinogenicity and the reproductive toxicity of MTBE. The document addressing the evidence relevant to carcinogenicity of MTBE contains an extensive discussion of the issues raised regarding the

appropriateness of the reporting and analysis of the bioassay data, and the relevance of the observed tumor sites to human cancer risk. We are submitting the October 1998 draft of this document, *Evidence on the Carcinogenicity of Methyl Tertiary Butyl Ether (MTBE)*, for your consideration. The Carcinogen Identification Committee met on December 10, 1998 and considered MTBE. Although a formal vote on MTBE was not taken by the Committee, a polling of the six members in attendance indicated that the four affirmative votes necessary for listing MTBE as causing cancer would not be forthcoming (three Committee members indicated that they would vote in favor of listing, three indicated they would not, and one member was not present).

If you would like additional information about OEHHA's activities related to carcinogen hazard identification or have specific questions about the enclosed OEHHA documents, please call Dr. Martha Sandy, Chief of the Cancer Toxicology Unit at (510) 622-3192.

Sincerely

George V. Alexeeff, Ph.D., DABT
Deputy Director for Scientific Affairs

Enclosures

GVA:ke

MTBE

(methyl tertiary butyl ether)

Briefing Paper
prepared by the

California Environmental Protection Agency

April 24, 1997

(updated March 30, 1998)

Table of Contents

I. EXECUTIVE SUMMARY 1

II. BACKGROUND 2

A. What is MTBE and Why Is It Used in Gasoline? 2
1. Description and Basic Properties 2
2. MTBE Usage and Production 2
3. Oxygenate of Choice in Reformulated Gasoline 3
4. Other Oxygenates 4

B. Requirements for Oxygenates 5
1. Federal Clean Air Act Amendments 5
2. California Wintertime Oxygenates Program 5
3. California Cleaner Burning Gasoline Requirements 6
4. Interaction of the Federal and State Gasoline Programs 7

C. MTBE's Role in Meeting Regulatory Requirements 7
1. Refineries Designed Around Use of MTBE 7

D. Emission Benefits of Cleaner Burning Gasoline 8
1. Criteria Pollutants 8
2. Toxic Air Contaminant Emissions 8
3. Exhaust and Evaporative MTBE Emissions 8
4. Exposure and Risk 8

E. MTBE in Other States 9

III. HEALTH EFFECTS OF MTBE 10

A. Air - Acute Inhalation Effects 10
1. Health Research 10
2. Epidemiology Studies, Surveys, and Literature Reviews 10
3. Chamber Studies 12

B. Air - Chronic Inhalation Effects 12

C. Water 12
1. Health Advisory Level - Status 12
2. Taste and Odor Thresholds 14
3. Ecotoxicity 14

IV. MTBE IN AMBIENT AIR AND POTENTIAL CANCER RISK 14

A. Ambient Levels 15

B. Potential Risk 15

V. MTBE IN WATER 16

A. Drinking Water Supplies in California 16

B. MTBE's Unique Characteristics in Water 16

C. Routes of MTBE into Water Supplies 16

D. MTBE Levels in Water 17
1. Shallow Groundwater 17
(a.) National 17
(b.) California 18
2. Drinking Water 18
3. Overall Perspective Regarding MTBE in Water 20

VI. ONGOING ACTIVITIES 21

A. World 21

B. Nationwide 21

C. California 22

REFERENCES 25

APPENDIX: List of Internet Addresses with Information on MTBE 27

Acknowledgments

This paper was prepared in a collaborative effort by the Air Resources Board, the State Water Resources Control Board, and the Office of Environmental Health Hazard Assessment. It was also reviewed by the Department of Health Services. Research scientists at Lawrence Livermore National Laboratory, the University of California, Berkeley, and the University of California, Los Angeles, provided comments that assisted in the preparation of the April 24, 1997 version of this paper.

Because the information on MTBE is rapidly evolving, this briefing paper will be updated periodically. The briefing paper is also available on the Internet at the following address: http://www.arb.ca.gov/cbg/pub/pub.htm.

Updates - March 1998

The following updates have been made to the September 2, 1997, version of this document:

Page:	Revisions
9:	A section was added discussing the use of MTBE in other states.
10:	The "Health Effects of MTBE" section was revised and updated.
18:	Information on underground storage tank sites was updated.
18:	Drinking water detections of MTBE were updated.
19:	The detection of MTBE in Glennville was described.
21, 22:	The "Nationwide" and "California Ongoing Activities" sections were updated.
25, 26:	A reference was added regarding the ozone reduction benefits of cleaner-burning gasoline. The draft National Science and Technology Council report and the National Research Council review of that report were added as references.
27:	A list of Internet addresses with information on MTBE was added.

MTBE (METHYL TERTIARY BUTYL ETHER)
BRIEFING PAPER BY THE
CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
MARCH 1998

I. EXECUTIVE SUMMARY

Methyl tertiary butyl ether (MTBE) is a chemical compound used in the blending of gasoline. It has been used in gasoline in the United States (U.S.) since the 1970s, principally as an octane booster. Since the early 1990s, it has been used in gasoline in over 15 states to meet federal Clean Air Act (FCAA) requirements for oxygenates in wintertime oxygenated gasoline (starting in 1992) and in federal reformulated gasoline (RFG) (starting in 1995). Because of its oxygen-containing properties, up to 15 percent by volume of MTBE (11 percent in California) is added to gasoline to promote more complete combustion and reduce exhaust emissions of carbon monoxide (CO) and reactive organic compounds.

Because of MTBE's many favorable properties, including its high octane rating, beneficial dilution effect on undesirable gasoline components, ease of mixing with gasoline, and ease in distribution, this chemical has become the oxygenate of choice by refineries manufacturing federal RFG and California Cleaner Burning Gasoline. Refiners have basically designed their refineries around the ability to use MTBE to meet reformulated gasoline requirements. Other oxygenates that can be used as gasoline blending components include other ethers and ethanol.

Because of its increased use over the last several years, MTBE is now being found in many areas of the U.S. in groundwater and reservoirs, and to a much lesser extent in drinking water supplies. While we do not yet have sufficient information to quantify reduction in leaks from upgraded underground storage tanks (USTs), significant improvements in leak rates should result from the replacement of thousands of leaking tanks with new double-walled tanks coupled with more accurate monitoring systems. Evidence to date has shown very little MTBE in drinking water outside of Santa Monica and Glennville. However, groundwater tends to move slowly and MTBE does not appear to adsorb to soil particles or readily degrade in the subsurface environment. Therefore, it is not possible to predict with accuracy whether MTBE from the many old leaking UST sites will affect deeper aquifers. Mitigation of leaking UST sites in close proximity to active drinking water supply wells may be necessary to avoid unreasonable risk. MTBE has not significantly impacted California surface drinking water resources, since when MTBE is present, concentrations are typically five to 10 times below the United States Environmental Protection Agency (U.S. EPA) draft health advisory limits.

Estimates of cancer inhalation potency developed by the U.S. EPA for the National Science and Technology Council report indicate there is a small potential risk of cancer due to breathing MTBE. In California, this risk is estimated to be one to two lifetime cancer cases

per million people exposed. This risk is very low in comparison to the substantial overall reduction in the estimated lifetime cancer risk of about 60 per million from the use of California Cleaner Burning Gasoline.

Currently, there is little information on the carcinogenic effects of exposure to MTBE by the oral route. Further research is also needed on systemic, reproductive, and developmental effects of both inhalation and oral exposures. The California Environmental Protection Agency (Cal/EPA) will continue to review current and proposed research designed to fill in these data gaps.

This briefing paper provides a summary of what we currently know about MTBE. It includes information on why MTBE is used, how much is used, legislative and regulatory requirements, the role of MTBE in meeting these requirements, and the benefits of Cleaner Burning Gasoline. Also included is an overview of health effects of MTBE in both air and water, and an overview of the information we have regarding MTBE in water supplies. We conclude with a discussion of ongoing activities to ensure that Californians' health and our environment is protected from MTBE contamination.

II. BACKGROUND

A. What is MTBE and Why Is It Used in Gasoline?

1. Description and Basic Properties

MTBE, whose molecular formula is $C_5H_{12}O$, is a synthetic chemical used as a blending component in gasoline. It is a colorless liquid at room temperature and is flammable.

MTBE has a high volatility (vapor pressure 245 mm Hg at 25° C) and a high octane value. MTBE is soluble both in gasoline and in water, which means it disperses evenly and stays suspended without requiring physical mixing.

MTBE has been used commercially in Europe as a gasoline blending compound since the early 1970s. As lead was phased out of gasoline in the U.S. in the middle and late 1970s, MTBE's use increased to boost the octane value of gasoline. MTBE was approved by the U.S. EPA in 1981 to be used in gasoline at levels up to 10 percent by volume. Subsequently, in 1988, the U.S. EPA approved the use of MTBE in gasoline at levels up to 15 percent by volume.

2. MTBE Usage and Production

Since the introduction of MTBE to raise gasoline octane in the late 1970s, MTBE usage in the U.S. has grown rapidly. The amount of MTBE used in the U.S. has increased from about 12,000 barrels per day in 1980 to about 250,000 barrels per day currently and

accounts for about 3 percent of the gasoline consumed in the U.S. Of the total MTBE used in the U.S., about

40,000 barrels per day are imported. The increase in MTBE usage has also been fueled by FCAA requirements, which mandate oxygenated gasoline during the wintertime to help meet standards for CO and which require oxygenates in reformulated gasoline throughout the year in areas with the most serious ozone air pollution.

MTBE is manufactured from isobutene, a product of petroleum refining. Of the total MTBE used in the U.S., approximately 80 percent is produced in the U.S. and about 20 percent is imported from other countries. Texas supplies about 80 percent of the MTBE produced in the U.S., with another 10 percent produced in Louisiana. California produces about 5 percent of the total U.S. production. California uses about 100,000 barrels per day of MTBE, about 85 percent of which is imported, primarily by ocean-going tankers.

Currently, MTBE is added to about 30 percent of the gasoline consumed in the U.S. and to virtually all of the gasoline consumed in California.

3. Oxygenate of Choice in Reformulated Gasoline

MTBE was chosen by refiners to meet the oxygenate requirement. Its high octane rating, ability to readily mix with other gasoline components, dilution of undesirable components (aromatics, sulfur, olefin and benzene), and distillation temperature depression make it a very desirable gasoline blending component. The high octane characteristic is particularly useful. Benzene and other aromatic compounds have traditionally been used to increase gasoline octane because of their high octane values. As reformulated gasoline regulations have required that aromatic and benzene levels of gasoline be reduced, refiners had to use other compounds to meet gasoline octane specifications. The use of MTBE has helped offset this loss and reduced emissions of a known human carcinogen (benzene).

In California, MTBE is blended into gasoline at about 11 percent by volume. Thus, total gasoline production is increased by 11 percent solely through the addition of MTBE. In California, this means about 100,000 barrels of our approximate 900,000 barrels daily gasoline demand is being met through the blending of MTBE into gasoline.

MTBE's use in gasoline reduces the concentrations of other compounds by the amount of MTBE added. Thus, 11 percent MTBE reduces the total aromatic, olefin, sulfur, and benzene content of gasoline by 11 percent, thereby providing a valuable role in meeting reformulated gasoline requirements for these compounds. MTBE usage also makes it easier for refiners to meet distillation temperature requirements for reformulated gasoline, due to its relatively low boiling point.

The blending of 11 percent MTBE into gasoline reduces the gasoline's T50 (the

temperature at which 50 percent of the gasoline evaporates) by 10 to 20 degrees Fahrenheit, and the T90 (the temperature at which 90 percent of the gasoline evaporates) by 2 to 6 degrees Fahrenheit, thus helping to meet the Cleaner Burning Gasoline requirements for T50 and T90.

Finally, MTBE readily mixes with other gasoline components and can be readily transported through the existing gasoline distribution system.

There is one clear disadvantage to the use of oxygenated gasoline. Oxygenates generally have a lower volumetric energy content than gasoline. Thus, oxygenates reduce the energy content of the gasoline to which they are blended. This reduction in the gasoline's energy content results in a reduction in a vehicle's fuel economy. The 3 percent reduction in fuel economy associated with reformulated gasoline is largely a result of the use of oxygenates. [1, 2, 3, 4]

There has been some confusion about the decrease in fuel economy negating the emission reduction benefits of the Cleaner Burning Gasoline regulations. The primary reason for the confusion is the relationship between emission reductions and the number of miles driven. Vehicle emission reductions associated with Cleaner Burning Gasoline are measured in grams per mile, and the cumulative emission reductions are dependent on total vehicle miles driven, not on gallons used.

4. Other Oxygenates

There are other oxygenates available for use as gasoline blending components. They include ethanol and other ethers/alcohols (ethyl tertiary butyl ether [ETBE], tertiary amyl methyl ether [TAME], and tertiary butyl alcohol [TBA]). Some of these are used in limited amounts in California. However, no other oxygenate has MTBE's unique combination of price and supply, gasoline blending, and transportation properties.

Ethanol, like MTBE, also has a high octane rating, acts as a diluent, and depresses the T50 and T90 temperatures. The T50 and T90 temperatures are important properties in defining how gasoline can affect engine performance (vehicle driveability). However, ethanol increases gasoline's Reid vapor pressure (RVP) and this, combined with its higher oxygen content, means less of it can be used as a gasoline blending component. Because less of it can be used, the overall volume enhancement, octane increase, diluent, and T50 and T90 depression benefits are less than for other oxygenates.

The use of ethanol also presents some blending and distribution-related problems not seen with MTBE and the other ethers. Ethanol has a high affinity for water. If a gasoline containing ethanol comes into contact with water, the water and ethanol will combine into a separate phase and separate from the gasoline. Because of this phase separation potential, ethanol and gasoline containing ethanol are not transported through pipelines where there is a

possibility of water being present. Therefore, when ethanol is blended into gasoline, the blending must be done at the terminals. Terminals in California are not currently equipped to handle a large amount of ethanol blending. A further complication is that most ethanol is currently produced in the midwest with no practical alternatives for importing to California except by rail.

ETBE and TAME are similar to MTBE in terms of the benefits they provide. However, ETBE and TAME provide less T50 depression benefits than MTBE and as a result they provide less flexibility to refiners in meeting the Cleaner Burning Gasoline T50 requirement. Also, there is currently much less production capacity for ETBE and TAME than for MTBE. Finally, there are fewer studies available on the toxicity and health effects of using ETBE and TAME, and it is unknown if these chemicals possess greater or lesser toxicity than MTBE.

TBA has an octane rating of about 100, about 10 numbers less than MTBE but still higher than most gasoline blending components. However, TBA increases the volatility of gasoline, or
its tendency to evaporate, so that the mixture of gasoline and TBA will not comply with reformulated gasoline specifications for gasoline volatility.

B. Requirements for Oxygenates

1. Federal Clean Air Act Amendments

The 1990 amendments to the FCAA require the use of oxygenates in areas with poor air quality, and are the driving force behind the extensive use of oxygenates. Since 1992, oxygenates have been required during winter months in areas with high CO levels. Since January 1995, the FCAA has required the use of oxygenates in federal RFG in 10 areas nationwide, and many other areas have voluntarily joined this program to reduce pollution. In California, the federal RFG requirements apply in almost all of southern California, and in Sacramento (two-thirds of statewide gasoline use occurs in these areas).

About 30 percent of the gasoline sold nationwide must meet the federal RFG requirements. The FCAA requires, among other things, that gasoline produced under the RFG regulations contain a minimum average oxygen content of 2 percent by weight. This corresponds to 11 percent MTBE by volume.

The 1990 amendments to the FCAA also included a requirement that states that are nonattainment for CO must use oxygenated gasoline. This program requires that gasoline in the wintertime must contain a minimum oxygen content of 2.7 percent by weight. The FCAA also allowed a state to require a lower oxygen content, if justified. Some 27 areas in the country have been using oxygenates (MTBE and ethanol) during the winter months.

2. California Wintertime Oxygenates Program

To comply with FCAA requirements for a wintertime oxygenate program in CO nonattainment areas, in 1991 the Air Resources Board (ARB) adopted its program requiring oxygen in gasoline during the winter months. However, because of the adverse effect of higher levels of oxygenates on oxides of nitrogen (NO_x) emissions, California requested an EPA waiver from the basic 2.7 percent oxygen (15 percent MTBE) requirement in the FCAA and only requires 1.8 to 2.2 percent oxygen (approximately 11 percent MTBE) in its winter gasoline.

In California, starting with the winter of 1992, all of California's wintertime gasoline (October through January) has been oxygenated, with MTBE comprising about 90 percent of the oxygenates used and ethanol the remaining 10 percent. The wintertime oxygenate requirement was originally adopted as a statewide requirement because about 80 percent of the gasoline used in the state was used in CO nonattainment areas. If the requirement was in effect only in the nonattainment areas, distribution problems would have arisen because of the regional nature of the state's gasoline distribution system and the lack of facilities necessary to segregate oxygenated gasoline from nonoxygenated gasoline. Also, motor vehicle travel patterns are such that implementing the requirement only in nonattainment areas would not maximize the benefits, since vehicles coming into nonattainment areas from attainment areas would contribute CO emissions.

Because of its fuels and mobile source programs, California is no longer experiencing exceedances of the ambient CO standard except for the greater Los Angeles area. The ARB has asked the U.S. EPA to redesignate other areas as attainment for CO. Once an area is redesignated, the FCAA continues to require a wintertime oxygenates program only to the extent the program is necessary to maintain attainment of the CO standard.

3. California Cleaner Burning Gasoline Requirements

In 1991 the ARB adopted its Cleaner Burning Gasoline regulations which became effective on March 1, 1996. The basic requirements of the regulations consist of specifications for eight gasoline properties. These properties are: RVP, benzene, aromatic hydrocarbon content, sulfur content, olefinic hydrocarbon content, T50, T90, and oxygen content.

Because of the oxygen requirements in the federal RFG program, the state's gasoline regulations include an oxygen content specification of 2 percent year round. However, a key element of the California program is a mathematical or "predictive" model that allows refiners to vary the composition of their gasoline as long as they achieve equivalent emission reductions. Except during winter months, and for areas not subject to federal RFG requirements, refiners can use the predictive model to reduce or even eliminate the use of oxygenates.

When the reformulated gasoline regulations were adopted, the concern over the use of oxygenates was not raised as an issue. Both ethanol and MTBE had been used in gasoline for

over 10 years. Also, the U.S. EPA had formally approved both oxygenates as gasoline additives in the 1980s.

4. Interaction of the Federal and State Gasoline Programs

Although they are exempt from many of the federal enforcement requirements, California refiners are subject to the underlying federal RFG standards as well as the state's requirements. Two-thirds of California's gasoline is subject to the federal minimum oxygen requirement. This means that, as a practical matter, the refiners cannot take full advantage of the California predictive model to produce gasoline with an oxygen content of less than 2 percent.

C. MTBE's Role in Meeting Regulatory Requirements

1. Refineries Designed Around Use of MTBE

Because of MTBE's beneficial properties as a gasoline blending component, California gasoline producers chose to configure their refineries and designed their gasoline compliance strategies based on using MTBE as a principal blending component. The size and type of the refinery process units that refiners built (over a three year period with a $4 billion investment) are structured to comply with the gasoline regulations through the use of MTBE. Even if the gasoline oxygen requirements were not in effect, most refiners have indicated they would still use large quantities of MTBE because of its beneficial volume enhancing, octane increasing, dilution, and distillation temperature depression effects.

As mentioned above, although there are other ether-type oxygenates available, we can assume that if MTBE was not acceptable the other ethers may not be acceptable. While ethanol can be used in reformulated gasoline, it is used at 6 percent volume, instead of 11 percent, and California would experience a reduction in gasoline production. Ethanol also interferes with meeting RVP requirements.

Without MTBE and other oxygenates, the amount of Cleaner Burning Gasoline being produced would be reduced from current levels. Refiners would lose the volume of the MTBE previously added and the other benefits, such as dilution effects, taken advantage of by refiners in complying with the specifications for Cleaner Burning Gasoline. Production capacity in California of complying gasoline would decrease significantly, until substantial additional refinery process equipment was added. Over the short-term, significant imports would be needed to make up the lost product volume. Over the long-term, refiners could upgrade and expand their production capacity. It is predicted that such a strategy would significantly increase the cost of gasoline in California.

The California Energy Commission has been directed by the Legislature to conduct a study of possible replacements for MTBE in gasoline, including TAME, ETBE, TBA, and

ethanol, costs associated with each alternative, and impacts on gasoline supply and price. Work will be completed this spring.

D. Emission Benefits of Cleaner Burning Gasoline

1. Criteria Pollutants

California Cleaner Burning Gasoline reduces emissions of ozone precursors (volatile organic compounds [VOC] and NO_x) from gasoline vehicles by about 15 percent (300 tons per day). This is the equivalent of removing emissions from 3.5 million vehicles from California's roads. CO emissions are reduced by about 11 percent (1300 tons per day) and sulfur dioxide (SO_2) emissions are reduced about 80 percent (30 tons per day). The emission reductions are essential for attainment of the air quality standards for ozone, CO and particulate matter. An analysis of air monitoring data indicates that the Cleaner Burning Gasoline program reduced ozone levels in Southern California and Sacramento by 12 percent and 11 percent, respectively.[5]

2. Toxic Air Contaminant Emissions

California Cleaner Burning Gasoline results in about a 50 percent (20 tons per day) reduction in exhaust benzene emissions and a 30 percent (1 ton per day) reduction in exhaust 1,3-butadiene emissions from gasoline powered motor vehicles. Evaporative benzene emissions from motor vehicles are reduced by about 60 percent (8 tons per day). Emissions of formaldehyde and acetaldehyde are increased by about 30 percent (2 tons per day) and 5 percent (0.1 ton per day), respectively, mainly as a result of adding oxygenates to gasoline. The oxygen-bearing MTBE (or any other oxygenate) is conducive to the formation of these oxygenated exhaust compounds. Ambient air monitoring has shown a 50 percent decrease in benzene levels statewide.

3. Exhaust and Evaporative MTBE Emissions

The increased use of MTBE in gasoline over the last 10 years has resulted in increases in MTBE emissions to the atmosphere. Statistical analyses of emissions data generated by the Auto/Oil Air Quality Improvement Research Program, the oil companies, ARB and others indicates a strong correlation between MTBE emissions and gasoline MTBE content. [6] For 11 percent MTBE gasolines, total exhaust MTBE emissions are about 2.5 percent of total hydrocarbon emissions. Evaporative MTBE emissions are about 8 to 10 percent of total evaporative hydrocarbon emissions. Collectively these emissions amounted to approximately 43 tons per day in California in 1996. Because of the state's overall emissions control programs identified in the California State Implementation Plan for Ozone, these levels are expected to be reduced to approximately 20 tons per day by 2010.

4. Exposure and Risk

The four toxic air contaminants associated with the burning of gasoline (benzene, 1,3-butadiene, formaldehyde, and acetaldehyde) all have different carcinogenic potentials, or potencies. Taking into consideration the relative quantities emitted, the greatest risk is posed by benzene, followed by 1,3-butadiene, formaldehyde, and acetaldehyde. An approximate estimate of the overall reduction in carcinogenic risk resulting from the Cleaner Burning Gasoline regulations can be made by weighing the reductions, or increases, in emissions of each compound with its relative potency. Performing this type of calculation shows that California's gasoline regulations achieve an overall reduction in carcinogenic risk of about 40 percent, due to the change in the relative contributions to risk of these four compounds. [7,8,9]

Using numbers developed by the U. S. EPA based on the most recent data, when the increase in MTBE emissions is included in the estimate of the reduction in carcinogenic risk, the overall risk reduction is still about 40 percent. [7] Using these data, there is a high reduction in exposure and risk with Cleaner Burning Gasoline even when adjustments based on the possible carcinogenicity of MTBE are made. It is also important to note that MTBE is only tentatively identified by the U.S. EPA as having a "human carcinogenic hazard potential," [10] whereas the other four compounds have been formally identified as probable or known human carcinogens.

No oral ingestion health studies are available for reproductive or developmental effects of MTBE in animals. However, inhalation studies in rats and mice did show some reproductive and developmental effects at doses 1,000 to 10,000 times higher than expected human exposures from ambient concentrations of MTBE. Thus, it is highly unlikely that adverse reproductive or developmental effects of MTBE would be observed in the general population.

E. MTBE in Other States

There is a public misconception that MTBE has been banned in certain other states, including Alaska and Montana. To our knowledge, no state has banned the use of MTBE in gasoline. Alaska's oxygenated fuels program was suspended pending the results of health studies (see page 10), but was later reinstated. While MTBE could be used in Alaska's wintertime fuel, the small size of the market along with market choices has resulted in the use of ethanol. Ethanol blended fuel has been dispensed in Alaska since January 1995. The City of Missoula, Montana, began using ethanol instead of MTBE in its oxygenated fuels program in the winter of 1993-94, but has not taken action which prohibits the use or sale of MTBE.

Several states have discontinued their winter oxygenated fuels programs because they are not needed to achieve or maintain their CO attainment status. North Carolina was able to demonstrate to the U.S. EPA that emission reductions from fleet turnover are sufficient to maintain the CO standard through the year 2005. North Carolina has not taken action which prohibits the use or sale of MTBE. New Jersey and Connecticut are planning to discontinue their wintertime oxygenated fuels programs in the 1998-99 winter season. However, because

of their ozone nonattainment status, these states remain subject to the federal RFG program year-round, and will continue to use MTBE in their gasoline.

Finally, a number of Western states (Washington, Oregon, Colorado, Nevada, Arizona, and New Mexico) are using ethanol in their wintertime fuels programs. However, their rules do not specify (or prohibit) the use of any particular oxygenate.

III. HEALTH EFFECTS OF MTBE

A. Air - Acute Inhalation Effects

1. Health Research

Recently, a substantial amount of health-related research has been conducted on MTBE. Based on these studies there is no evidence that MTBE at ambient concentrations causes acute health effects. Approximately 20 studies in animals and humans have been conducted since 1987. Possible acute effects of MTBE include complaints such as nausea, headaches, dizziness, rashes, and spaciness. Allegations about these effects have been investigated in "retrospective" epidemiology studies of individuals who complained of headaches, dizziness, and respiratory problems after introduction of oxygenated gasoline; in human subjects exposed to a known amount of MTBE in chamber studies; from the analysis of health surveys of workers exposed to MTBE in the workplace; and literature reviews. None of these studies have demonstrated a causal association between MTBE exposure at ambient or occupational levels and alleged acute effects (but see discussion below). The following section provides details of those studies. Please note that only key studies are reviewed and the discussion is not meant to be an exhaustive review of the literature on MTBE and health effects.

2. Epidemiology Studies, Surveys, and Literature Reviews

Several studies undertaken over the past four to five years were unable to find any correlation between reported acute health effects and MTBE exposures experienced by the general public from MTBE's use in gasoline.

In the winter of 1992, the state of Alaska began using 15 percent MTBE in wintertime oxygenated gasoline as part of the federal requirements to reduce emissions of CO in Fairbanks and Anchorage. There were reports of headaches, dizziness, nausea, and spaciness after refueling and/or working around oxygenated gasoline. The Centers for Disease Control (CDC), U.S. EPA, and the state of Alaska investigated these complaints but were unable to associate them with MTBE exposure. Instead, it was suggested that the increase in price of the new federal RFG, the odor of MTBE, and harsh climate of Alaska resulted in some of the public associating changes in fuel with the reported symptoms.

In 1993, the Environmental and Occupational Health Sciences Institute (EOHSI) surveyed New Jersey garage workers, some of whom were exposed to MTBE, and some of whom were not. No significant differences in the frequency of reported symptoms were observed between the two groups.

Milwaukee, Wisconsin began to use MTBE in its gasoline as part of the federal RFG program in November 1994. Similar health complaints, as voiced in Alaska, were registered in Wisconsin. The U.S. EPA, Wisconsin Department of Health, CDC, and the University of Wisconsin investigated complaints from approximately 1500 people. They wrote two reports (May and September 1995) [11,12] and concluded that they could find no relationship between reported health effects and MTBE exposure. It was suggested that the odor of MTBE, increase in price of wintertime gasoline, and negative media coverage were responsible for the reports of health problems associated with exposure to gasoline.

Three additional, major literature reviews on the acute health effects of MTBE have been conducted. Reviews from public health agencies in Maine (1994) [13] and Connecticut (1995) [14] and the Health Effects Institute (HEI) (1996) [15] could find no acute health effects associated with exposure to MTBE from gasoline use.

In response to the negative publicity associated with the use of federal wintertime oxygenated fuel, the White House Office of Science and Technology Policy in September 1995 directed federal agencies to review fuel economy and engine performance issues, water quality, air quality benefits, and health effects of oxygenates in fuel. The National Science and Technology Council (NSTC) issued a draft report [16] which, along with the HEI report mentioned previously, was reviewed in March 1996 by the National Research Council (NRC) of the National Academy of Sciences. [17] The NRC found that, while largely anecdotal, the occupational studies cited in these reviews "are consistent with the studies of Alaska, Connecticut, and New Jersey, all of which reported that workers who are exposed to higher levels of MTBE may experience symptoms due to those exposures...The committee believes that while the epidemiologic data currently available do not establish a causal relationship between exposure to gasoline containing MTBE and the development of symptoms, these findings do indicate that some people have experienced acute symptoms associated with exposure to gasoline containing MTBE."

In their June 1997 final report [10], the NSTC concluded that with the information collected to date, there was no evidence that MTBE is causing increases in acute symptoms or illnesses at concentrations experienced by the general population, but anecdotal reports of acute health symptoms among some individuals cannot yet be explained or dismissed. The NSTC also recommended that greater attention should be given to the potential for increased symptom
reporting among workers exposed to high concentrations of oxygenated gasoline containing MTBE.

Regarding the issue of acute sensitivity to MTBE, the NRC, in their 1996 review of the draft NSTC report, concluded that there was no reason to believe that some people have extreme sensitivity to MTBE. The final NSTC report concluded that "an examination of possible predisposing factors might be useful to better understand the occurrence of various symptoms in the general public following exposure to MTBE-containing gasoline."

3. Chamber Studies

In 1993, Yale University and the U.S. EPA, in two separate studies, exposed individuals to clean air and air with MTBE. No increase in acute symptoms was observed in individuals exposed to MTBE at concentrations that would be encountered while refueling a car.

The EOHSI is conducting a study on individuals who have reported a sensitivity to MTBE and recruited from the "Oxybuster" group in New Jersey. The Oxybusters is a citizens' group which claims their members experience acute health effects from breathing MTBE at ambient concentrations. Those individuals are being exposed to gasoline with and without MTBE. Results are expected later in the year.

B. Air - Chronic Inhalation Effects

Animal evidence suggests that MTBE may be a weak carcinogen. The petrochemical industry and U.S. EPA reviewed the results of a $3.5 million study on mice and rats exposed by inhalation to MTBE. At high concentrations, rats exhibited kidney lesions and tumors, and mice developed liver tumors. These data implied that MTBE may be a weak carcinogen and the
U.S. EPA has indicated that MTBE could be considered as "having a human carcinogenic hazard potential." [10] The U.S. EPA evaluated the data and calculated two unit risk numbers: 7.5×10^{-8} per $\mu g/m^3$ based on the mouse liver tumors and 1.7×10^{-7} per $\mu g/m^3$ based on the rat kidney tumors. For comparison purposes, potency values for benzene and 1,3-butadiene are 2.9×10^{-5} per $\mu g/m^3$ and 1.7×10^{-4} per $\mu g/m^3$, respectively, or 170 to 2,100 times the potency estimates for MTBE.

C. Water

1. Health Advisory Level - Status

The following is a history and the scientific basis of the California and U.S. EPA health advisories which have been proposed for MTBE in water. A "health advisory" is a level (or range of levels) for drinking water which, if exceeded, the water supplier is advised to find another source of drinking water. It is not a regulatory or enforceable cleanup number. (Those numbers are called Maximum Contaminant Levels or MCLs.) Health advisories are set for compounds which are found in drinking water supplies and for which there are no

existing MCLs.

In 1991, the Department of Health Services (DHS) requested the Office of Environmental Health Hazard Assessment (OEHHA) to develop an action level for MTBE in water. (An action level is analogous to a health advisory.) In response, an interim action level of 35 parts per billion (ppb) was proposed by OEHHA based on the U.S. EPA's reference dose (RFD). The RFD applies a 10,000-fold safety factor to a subchronic animal lowest observable adverse effect level (LOAEL).

In 1993, the U.S. EPA developed a draft long-term health advisory for MTBE in drinking
water of 20-200 ppb based on a subchronic drinking water toxicity study in mice. The reason for the range is the uncertainty regarding the carcinogenic potential of MTBE.

In 1995, DHS requested OEHHA to review MTBE again and set an action level that would replace the interim action level recommended by OEHHA in 1991. Rather than devote limited OEHHA resources to an independent analysis, OEHHA and DHS agreed to wait until the
U.S. EPA update is completed.

In the early 1990s, Dr. Cesare Maltoni of the Bologna Institute of Oncology conducted a large scale experiment of MTBE exposure in rats by the oral route. Dr. Maltoni reported data for combined leukemias and lymphomas in female rats and testicular tumors in male rats. While the National Toxicology Program recommends against combining leukemias and lymphomas in F344 rats in developing cancer potencies, Dr. Maltoni observed leukemias and lymphomas in the female Sprague-Dawley rat. The NRC, in their 1996 review of the HEI and draft NSTC reports, recommended that Dr. Maltoni's findings be peer reviewed by the U.S. EPA. Dr. Maltoni has not yet set a date for that review.

In December 1996, the U.S. EPA released a draft Longer-Term Health Advisory of 70 ppb for public comment which would replace the 20-200 ppb range set in 1993. This analysis was based on a 90-day study of effects of MTBE by ingestion in rats. The U.S. EPA's Office of Water was unable to include the Maltoni data in the development of a Lifetime Health Advisory because of lack of peer review of the underlying data.

In December 1997, the U.S. EPA's Office of Water released a new Drinking Water Advisory for MTBE of 20-40 ppb. The new advisory addresses odor and taste detection levels but also establishes a large margin of safety for health effects. The U.S. EPA may apply a physiologically based pharmacokinetic (PBPK) model, when it becomes available, to existing animal inhalation data to develop an equivalent oral cancer potency slope and Lifetime Health Advisory for water.

Recently signed legislation (Assembly Bill [AB] 592, Kuehl, and Senate Bill [SB]

1189, Hayden) requires DHS to develop a primary (health-based) drinking water standard for MTBE by July 1, 1999. By summer 1998, OEHHA will adopt a Public Health Goal for MTBE in drinking water. DHS uses Public Health Goals adopted by OEHHA in developing drinking water standards.

2. Taste and Odor Thresholds

Previous investigations have reported taste (24-135 ppb) and odor (15-180 ppb) threshold ranges for MTBE in water. The Metropolitan Water District of Southern California recently completed a study to determine the aesthetic effects of MTBE in drinking water. The threshold level at 60 percent probability ranged from approximately 25-60 ppb for taste and 40-70 ppb for odor at 25°C. Since this represents the threshold level at 60 percent probability, the more sensitive people would most likely detect MTBE in drinking water at much lower levels. The authors of the study stated that future research using a broader subject base is needed in order to extrapolate the threshold ranges to be representative of the general public. However, the U.S. EPA noted that data from this study were consistent with those of two other studies, which collectively supported a range of 20-40 ppb as an approximate "threshold" for taste and odor responses. The U.S. EPA noted that human responses vary depending upon the sensitivities of the particular individual and the site-specific water quality conditions, and that some people may detect MTBE below this range. Indeed, detection levels as low as 2.5 ppb (odor) and 2.5 ppb (taste) have been reported.

AB 592 and SB 1189 require DHS to develop a secondary taste and odor drinking water standard for MTBE that does not exceed consumer acceptance levels. DHS is planning to propose a secondary standard as low as 5 ppb in early 1998 and seek public comment so that it can adopt a final standard by July 1, 1998.

3. Ecotoxicity

Concern has been raised about the effects of MTBE in water on plants and animals. However, the species tested so far for short-term toxicity have high (mg/L) thresholds for effects of MTBE. The levels tested are in the range of 100-1000 mg/L and the species tested include green alga, tadpoles, shrimp, minnows, and rainbow trout. Research by the American Petroleum Institute and others on ecological hazards of MTBE exposure is continuing. Because of the high rate of MTBE usage in California, MTBE's high water and lipid solubility, and lack of information on toxic effects of long-term exposure (e.g., reproductive impairment), Cal/EPA has a continuing interest in reviewing current and proposed research to fill in these data gaps.

IV. MTBE IN AMBIENT AIR AND POTENTIAL CANCER RISK

As discussed below, ambient air concentrations and health effects data suggest the

70-year lifetime potential cancer risk from MTBE air exposures is typically one to two per million. This is in contrast to general ambient cancer risks in California which average about 250 per million statewide from air toxics (based on ambient monitoring of compounds with cancer potency factors). New increases in air exposures typically become a concern at the 10 per million risk level. The very slight increase in risk from MTBE in ambient air is overwhelmingly offset by the reduced cancer risk from the use of California Cleaner Burning Gasoline.

A. Ambient Levels

Ambient levels of MTBE in California are similar or slightly higher than limited data suggest for other states. In 1985, the ARB established a 20 station toxic air contaminant air monitoring network. This network is the most comprehensive in the world and has led the way for development of analytical methods to detect low levels of toxic air contaminants.

California began analyzing ambient air for MTBE in 1996. Preliminary data suggest a statewide average will be approximately 2 ppb with higher concentrations in the South Coast of about 4 ppb. The limit of detection is 0.2 ppb.

MTBE has an atmospheric lifetime of four days and its primary byproducts are tert butyl formate and formaldehyde. Other byproducts include acetic acid, acetone, and TBA. It is not expected that ambient concentrations of these byproducts would pose a significant health risk.

The Desert Research Institute, under contract to ARB, monitored for MTBE from July to September of 1995 and 1996 in Southern California, at the Azusa, Burbank, and North Main monitoring sites. The monitoring was designed to measure peak morning rush hour concentrations (6 to 9 a.m.), and was part of a comprehensive study to analyze reactive organics in the South Coast Air Basin. The results showed a mean of approximately 4 ppb with a range of 1-11 ppb. These concentrations are similar to the ARB findings. Although the ARB sampled for 24 hours, because MTBE is a tailpipe pollutant, the highest concentrations are seen in the morning rush hour traffic.

The Bay Area Air Quality Management District (BAAQMD) has an 18 station network and has been monitoring for MTBE since 1995. The average concentration of MTBE in the BAAQMD is approximately 1 ppb.

There are only a few other areas in the country which have reported MTBE concentrations in ambient air. Fairbanks, Alaska reported concentrations ranging from 2-6 ppb when the gasoline contained 15 percent MTBE. Reports of MTBE concentrations as high as 2.6 ppm were reported in the breathing zone of individuals using self-service gasoline stations without vapor recovery equipment.

B. Potential Risk

As explained above, there has been no causal association established between ambient MTBE exposure and acute risk. For chronic risk, there are no "approved" unit risk numbers for MTBE. However, if we use the U.S. EPA unit risk numbers of 7.5×10^{-8} per $\mu g/m^3$ and 1.7×10^{-7} per $\mu g/m^3$ for a 70-year lifetime exposure, and a statewide exposure number of approximately 2 ppb (equivalent to 7.2 $\mu g/m^3$), the resulting risk indicates one potential lifetime cancer case per million. Since the concentrations of MTBE in ambient air in the South Coast appear to be about double the statewide average, we estimate that the potential cancer risk is about two per million in Southern California.

V. MTBE IN WATER

Cal/EPA and other state agencies have taken a proactive approach toward investigating MTBE in water in California. The primary release of MTBE into groundwater is from leaking USTs. Recreational boating is thought to be the primary source of MTBE in surface water.

A. Drinking Water Supplies in California

Sources of drinking water include: 1) surface water such as rivers, lakes, and reservoirs and 2) groundwater. According to the DHS Division of Drinking Water and Environmental Management, surface water and groundwater sources each provide approximately half of California drinking water supplies. Municipal drinking wells normally draw water from deep levels (200-400 feet) which may be protected over time from contamination migration depending on site-specific hydrogeologic conditions. It is the shallow, subsurface groundwater which is routinely contaminated by metals, pesticides, leaking USTs, etc. Therefore, shallow groundwaters are not used as a major supply source of municipal drinking water. However, private domestic and small community wells may use more shallow groundwater that can be vulnerable to contamination. Small community water systems, like larger public water supply systems, are all now required by DHS to monitor for MTBE. Only private domestic wells (which supply less than 1 percent of California drinking water) are not regulated at either the state or local level. Some private domestic well owners are voluntarily sampling their wells for MTBE.

B. MTBE's Unique Characteristics in Water

MTBE, unlike other hydrocarbons in gasoline, is very water soluble and poorly adsorbed to soils. [18] Thus, it moves with the groundwater flow, largely unretarded. MTBE also resists
biodegradation and little is known about its half-life in water. When it does degrade, the primary byproduct is TBA.

C. Routes of MTBE into Water Supplies

Gasoline constituents, including MTBE, can leak into sources of water from leaking USTs, leaking pipelines, spills or exhaust from recreational boats and personal watercraft, such as jet skis, and as a result of accidents during transport of fuel. The long-term potential for serious environmental impact is less from catastrophic failures because these failures trigger massive emergency response efforts, while other unknown and unmonitored discharges may remain unmitigated for many years.

In addition, atmospheric MTBE can dissolve in rainwater and enter surface water through storm water runoff. However, atmospheric sources have been found to result in low concentrations of MTBE in water relative to point sources such as USTs. [10]

MTBE can be expected to be found in groundwater at several thousand UST sites throughout California. Most of these sites are underlain with unused shallow groundwater. The concentration of MTBE at many of these sites is high (in the ppm range).

To address questions on the fate and transport of MTBE, the Lawrence Livermore National Laboratory (LLNL) is conducting research in the field and using mathematical models. A final report is due in March 1998. Also, research by the American Petroleum Institute is underway on the ecotoxicity of MTBE. Preliminary observations indicate the threshold for effects for aquatic organisms is high.

Concentrations of MTBE in surface water reservoirs with recreational boating range from <1-15 ppb (see page 19) and can be expected to be much higher in localized areas of boating activity, such as marinas. Drinking water intakes for marinas could occasionally receive spikes of MTBE from such boating activity and from the pipelines which provide fuel to the marinas.

Where surface water reservoirs supply drinking water to metropolitan areas, MTBE concentrations would be reduced by lake-wide dilution. However, there is no information on the half-life of MTBE in a reservoir and it is possible that lake-wide concentrations with high boating activity will increase over time, particularly during drought conditions where flushing from annual rainfall is reduced.

D. MTBE Levels in Water

California has considerable information about MTBE in its water supplies. This is due in large part to the proactive efforts of the ARB, the State Water Resources Control Board (SWRCB), the State Regional Water Quality Control Boards, and the DHS.

What follows is a summary of what we know today about MTBE levels in shallow groundwater, drinking water (including groundwater wells and reservoirs), and publicly

owned treatment works (POTWs).

1. Shallow Groundwater

(a.) National

The United States Geological Survey (USGS) has published the results of the National Water Quality Assessment (NAWQA) program.[18] This program analyzed concentrations of 60 VOCs from 198 shallow wells and 12 springs in eight urban areas (none in California) and 549 shallow wells in 21 agricultural areas (including the San Joaquin Valley). MTBE was detected in 27 percent of the urban wells and springs and 1.3 percent of the agricultural wells. MTBE was
the second most frequently detected VOC (behind chloroform) in urban wells. These are not drinking water wells, but rather monitoring wells, some of which were installed for the purposes of the study. No MTBE was detected in 100 agricultural wells in the San Joaquin Valley.

(b.) California

In June 1996, the SWRCB asked local regulatory agencies to require analysis at all leaking UST sites with affected groundwater. MTBE has been detected at the majority of the sites. Concentrations of MTBE in shallow groundwater near the source of the fuel release can exceed 100,000 ppb.

California has an aggressive UST replacement program underway to avoid future fuel leaks. State and federal statutes and regulations require that all USTs be removed, replaced or upgraded to meet current standards by December 22, 1998. Approximately 50 percent of the approximately 65,000 USTs now meet state and federal upgrade requirements. Upon completion of the program, the leaking of gasoline components, including MTBE, into soil and groundwater should greatly diminish.

2. Drinking Water

In 1995, the ARB requested the DHS Division of Drinking Water and Environmental Management to test for MTBE in the state's drinking water. In February 1996, DHS sent an advisory letter to water suppliers it regulates, requesting voluntary testing for MTBE while a monitoring regulation was being developed. The regulation was adopted on February 13, 1997, and requires monitoring of MTBE as an "unregulated chemical." This term refers to the fact that there is no established regulatory or enforceable drinking water level or MCL for MTBE. Water suppliers will be monitoring and reporting MTBE from sources of drinking water (DHS defines a drinking water source as either a drinking water well or a surface water intake) at least once every three years.

As a consequence of the 1996 DHS advisory, water suppliers began to voluntarily test for MTBE. As of February 1998, approximately 2,600 drinking water sources have been sampled and reported. Only 34 sources, nine of which are reservoirs, have reported detectable concentrations of MTBE. Two sources, Santa Monica and the City of Marysville (up to 115 ppb in January 1997), have reported concentrations above the U.S. EPA taste/odor drinking water advisory level of 20-40 ppb. Otherwise, the range of reported values was <1-15 ppb. Monthly updates on the results of the monitoring required by the DHS regulation are available on the Internet at:
http://www.dhs.ca.gov/org/ps/ddwem/publications/chemicals/mtbe/mtbsummary.htm.

In Santa Monica, two well fields (Charnock and Arcadia) have been contaminated with MTBE. These well fields used to supply 80 percent of the drinking water to Santa Monica. Concentrations as high as 610 ppb were observed in the Charnock aquifer and the seven wells in the field have been closed. This aquifer is in sandy soil vulnerable to contamination, and is surrounded by numerous USTs with two pipelines running directly through the field. Shell and Chevron have reached an agreement with the City of Santa Monica to pay for replacement water and past investigation costs. The City of Santa Monica is also working with five major oil companies discussing remediation of the water. In the Arcadia well field, two wells have been closed due to contamination from a UST at a nearby Mobil gasoline station. The City of Santa Monica filed a lawsuit charging "gross and willful negligence" on the part of Mobil. On February 19, 1997, Cal/EPA announced that the Los Angeles Regional Water Quality Control Board and Mobil Corporation had signed an agreement to clean up the gasoline-contaminated groundwater and secure a replacement supply of clean water. The agreement also requires Mobil to reach an agreement with the City of Santa Monica which provides for interim payments for past and future costs of replacement drinking water for the Arcadia well field.

Several private drinking water wells in Glennville, California were recently discovered to contain high concentrations of MTBE. In 1987, a leaking UST at the town's only gas station was replaced with a new double-walled tank. Although the tank was replaced, the soil and groundwater remained contaminated. In 1997, the Central Valley Regional Water Quality Control Board (CVRWQCB) sampled domestic and previously installed monitoring wells and found some of them were contaminated with MTBE (up to 430,000 ppb) and benzene (up to 22,000 ppb). Observing these high levels of MTBE, the CVRWQCB suspected a more recent leak from the tank that had replaced the original tank in 1987. Residential drinking water wells were contaminated with MTBE at reported levels of 5, 100, 120, 730, and 20,000 ppb. The latter well also contained 84 ppb of benzene. The CVRWQCB has indicated that the likely source of MTBE is the UST and associated piping installed in 1987, and is evaluating the possibility of using an alternative drinking water source.

Reservoirs in which MTBE has been detected through the DHS monitoring program include: Whiskeytown Lake and Lake Shasta in Redding; San Pablo and Cherry reservoirs in

the San Francisco Bay area; Lake Perris in the Los Angeles MWD; Canyon Lake in the Elsinore Valley MWD; Clear Lake in the Konocti County Water District; and Del Valle and Patterson Pass reservoirs in Alameda County. Other lakes and reservoirs in which MTBE has been detected include: New Don Pedro in the San Francisco Bay area; Coyote and Anderson in the Santa Clara Valley Water District; Modesto in the Stanislaus Water District; Castaic in the Los Angeles MWD; Lake Berryessa in Solano County; Donner Lake; and Lake Tahoe. MTBE concentrations range from <1-15 ppb, although Lake Shasta had 88 ppb in a surface water sample next to a houseboat at a marina dock in September 1996. All of these lakes and reservoirs allow gasoline power boat activity. Consequently, unburned MTBE from exhaust, as well as leaks and spills from marina gasoline storage, are likely sources of MTBE contamination. The sampling of Lake Shasta was designed to seek "worst cases" (surface water sheens) rather than average concentrations in the lake. Other gasoline constituents (e.g., benzene, toluene, ethylbenzene, and xylenes) were found in lower concentrations than MTBE. The City of Shasta Lake domestic water supply intake was also sampled in September 1996. Low MTBE concentrations (0.6 ppb) were found.

MTBE has been studied in lakes and reservoirs with recreational watercraft activity. Water was analyzed for hydrocarbons before and after organized jet ski events held in the summer and fall of 1996 in Orange County and Lake Havasu. MTBE was measured in the water at the small holding basin in Orange County at concentrations of up to 40 ppb a few days after the event even while there was negligible benzene, toluene, and ethylbenzene (classic markers of gasoline contamination). At the larger Lake Havasu, the MTBE concentrations increased from below the level of detection to 13 ppb near the surface.

The Carson POTW in Carson, California has also reported MTBE in its waste water. The Carson POTW processes the largest volume of refinery waste water in the nation (13 refineries sporadically discharge waste water to the POTW). Refineries in California perform their own pretreatment prior to discharging to sewers. The refineries' discharges contain average levels from 1-7 ppm with concentrations occasionally as high as 40 ppm.

California refineries are situated mainly along the coast and discharge directly or indirectly to marine waters. We currently lack information concerning impacts of relatively high concentrations of MTBE discharge (up to 40 ppm) on coastal marine life. Further studies of such
potential impacts are needed. No California refineries discharge their waste water to sources of drinking water.

3. Overall Perspective Regarding MTBE in Water

Only two municipal drinking water suppliers, Santa Monica and California Water Service (Marysville), and several private wells (Glennville) have detected MTBE at levels that required source closure. However, groundwater tends to move slowly and MTBE does not appear to adsorb to soil particles or readily degrade in the subsurface environment. Therefore,

it is not possible to predict with accuracy whether MTBE from the many old existing leaking UST sites in California will affect deeper aquifers. Mitigation of leaking UST sites in close proximity to active drinking water supply wells may be necessary to avoid unreasonable risk. With the continued replacement and upgrading of USTs, releases of hydrocarbons to groundwater should greatly diminish and minimize the potential for future MTBE contamination of groundwater.

Concerns have been raised over the presence of MTBE in lakes, reservoirs, and rivers where boating activity occurs. It is unknown how long MTBE will remain in the water. Later this year, more information on the persistence of MTBE in water should be forthcoming. The introduction of MTBE and other petroleum hydrocarbons to the aquatic environment can be reduced by best management practices such as minimizing leakage and spillage at marina tanks, piping, and fuel dispensing facilities. However, these latter potential sources of MTBE contamination are minimal compared to boats and personal watercraft.

As stated previously, the ambient air concentrations of MTBE result in the vast majority of current human exposures to MTBE and its associated risk. The current average ambient concentration in California is approximately 2 ppb. To receive an equivalent exposure from MTBE-contaminated drinking water, water concentrations of MTBE would have to average about 70 ppb. However, all data collected to date suggest drinking water concentrations from nondetect to very low (outside of Santa Monica, Marysville, and Glennville). Thus, at present it seems clear that the majority of health risks associated with MTBE are due to airborne exposures.

VI. ONGOING ACTIVITIES

A. World

The World Health Organization has just issued the second draft of an environmental health criteria document on MTBE. In it they state that carcinogenic findings in animal bioassays seem to warrant some concern of potential carcinogenic risk to humans, but the document does not contain a risk characterization.

B. Nationwide

The U.S. EPA is active in several areas including evaluations of health and water contamination. First, Article 211 of Title III of the Clean Air Act Amendments of 1990 requires that gasoline inhalation studies be conducted by oil companies. Animal research will focus on short and long-term inhalation effects of conventional gasoline and gasoline with MTBE. The Article 211 studies will also include human exposure research. The research will be completed at varying intervals over the next five years.

Regarding drinking water activities, the U.S. EPA's Office of Water just released a

new Drinking Water Advisory for MTBE (see page 13). In addition, MTBE is included in the Drinking Water Contaminant Candidate List required by the Safe Drinking Water Act. The list was published in February 1998, with final decisions on whether to establish a standard on at least five contaminants to be made by August 2001. In the interim, the Office of Water has initiated a database based on voluntary reporting from some states, USGS data, and other available sources.

The U.S. EPA's Office of Research and Development is working to identify MTBE research needs, including monitoring, exposure, health effects, and remediation. A workshop was held in early September to present an initial assessment of research needs to industry and academic groups. A draft report will be issued for public comment in spring 1998.

Other U.S. EPA activities include development of a protocol to collect data on potential CO reductions using federal oxygenated gasoline.

The HEI is funding three new studies designed to answer key questions on the metabolism of MTBE and other ethers in animals and humans.

C. California

Ongoing state government activities include: collection of ambient air data to characterize statewide levels, seasonal variations, and trends; enforcement of the DHS regulation requiring water suppliers to analyze municipal water for MTBE; and continued development of UST site clean up policy. In addition, the ARB is funding a study of in-vehicle exposure to VOCs, including MTBE. A final report is anticipated by fall of 1998.

The California Energy Commission is conducting a detailed evaluation of possible replacements for MTBE in gasoline, costs associated with each alternative, and impacts on gasoline supply and price. Work will be completed this spring.

Recently signed legislation (AB 592 and SB 1189) requires the development of primary (health-based) and secondary (taste and odor) drinking water standards for MTBE by July 1, 1999, and July 1, 1998, respectively. DHS is planning to propose a secondary standard as low as 5 ppb in early 1998 and seek public comment so that it can issue a final standard by July 1, 1998. DHS has also requested OEHHA to adopt a Public Health Goal under the California Safe Drinking Water Act (1996) for MTBE that can be used to develop the primary drinking water standard.

OEHHA has issued a request for information on the carcinogenicity and reproductive toxicity of MTBE as an initial step for consideration under the Proposition 65 listing process. AB 592 and SB 1189 require the Proposition 65 Science Advisory Board to recommend whether MTBE should be listed as a carcinogenic or reproductive toxin by January 1, 1999. Further information is available on the Internet at: http://www.calepa.cahwnet.gov/oehha.

Other recently signed legislation (SB 521, Mountjoy) requires the University of California to conduct a study of the health and environmental risks and benefits of MTBE in gasoline, as compared to ETBE, TAME, and ethanol. A report on the study is due to the Governor by January 1, 1999.

In addition to signing these bills, the Governor has directed the SWRCB to evaluate data on new storage tanks to determine if they are leaking and to evaluate refueling facilities and practices at marinas for possible modifications.

Local activities include the responsible parties' ongoing investigations, under the oversight of the Regional Water Quality Control Board (RWQCB), the U.S. EPA, and the City of Santa Monica, of the MTBE contamination which resulted in the closure of the City's Arcadia and Charnock drinking water well fields. There are more than 20 "possible" sources of contamination at the Charnock well field, however, the exact sources have not been completely confirmed. Without an admission of responsibility, Shell and Chevron have entered into a voluntary agreement with the City to replace the Charnock drinking water supply, and work cooperatively with the City to investigate contamination at the Charnock well field and implement a remediation program. The agreement, which is temporary and requires renewals through January 6, 2000, stipulates the cleanup of the drinking water to the lesser of 20 ppb or a more stringent regulatory standard, and requires the City and Shell/Chevron to work with the U.S. EPA and RWQCB to bring other companies into the agreement. Activities currently underway at Charnock include pipeline testing, a regional hydrology study, individual site investigations, joint U.S. EPA/RWQCB enforcement action, and a treatment technology evaluation.

The MTBE release impacting the Arcadia well field probably came from an adjacent Mobil service station. On March 18, 1998, Mobil entered into a voluntary agreement with the City to replace the Arcadia drinking water supply, and work cooperatively with the City to investigate contamination at the well field and implement a remediation program. The agreement was modeled after the Charnock agreement, and requires Mobil to pay $2.2 million for the City's past costs, including the cost of replacement water; cleanup of the drinking water to the lesser of 20 ppb or a more stringent regulatory standard, which must be met for one year without treatment before Mobil's cleanup obligations are satisfied; and a prohibition on the use of hazardous materials at the former Mobil service station property. Actions currently underway at Arcadia include a detailed groundwater investigation, decommissioning of the station, treatment of extracted groundwater from the Shallow Aquifer, and a treatment technology evaluation for drinking water.

It is unknown exactly when the well fields will be returned to production, however, Santa Monica, Mobil, Shell, and Chevron are committed to the restoration of the Charnock and Arcadia well fields, and the ongoing protection of the City's groundwater resources.

The City of Santa Monica, Association of California Water Agencies (ACWA), Western States Petroleum Association (WSPA), and Oxygenated Fuels Association (OFA) are working together on a research partnership to evaluate treatment technologies for MTBE in drinking water and source water protection measures. A memorandum of understanding, which will establish the partnership, identify research objectives, and specify funding commitments, is expected to be completed in June 1998. WSPA and OFA have agreed to provide $600,000 to fund this research in 1998, and additional funding is being sought from the U.S. EPA, U.S. Department of Energy (U.S. DOE), and other sources.

To gather more information about the impact of MTBE from California USTs, the LLNL has been funded by the SWRCB, U.S. DOE, and WSPA to characterize the fate and transport of MTBE to define plume migration in soil and groundwater and potential remediation technology. Findings to date indicate that in plumes, total hydrocarbon and benzene concentrations are not predictive of MTBE concentrations. A final report is due March 1998.

ACWA conducted an extensive study of California surface water reservoirs during the 1997 summer boating season. Preliminary data show that MTBE is being detected on the surface of reservoirs and near boat landings. Much lower levels are being reported at water intakes. A report on the survey is due to be completed in early 1998.

The Los Angeles County Sanitation District is studying the control of VOCs (including MTBE) at the Carson POTW. One goal of the study is to determine the scope of MTBE releases (both air and water) and to investigate bioremediation filter technology. A test biofiltration grid of composted sludge is effectively removing volatilized MTBE. However, the POTW estimates that most of the MTBE remains dissolved in the waste water. Research is also underway at the University of California, Davis to investigate bioremediation of MTBE. Although still in the pilot stages, development of a biofilter holds promise.

Finally, the USGS is conducting urban land use studies this year to characterize VOCs, including MTBE contamination. This is part of the larger national NAWQA program.

Questions regarding this document may be referred to the Cal/EPA Communications Director at
(916) 324-9670.

REFERENCES

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4. Data from California State Automobile Association on Fuel Economy, August 1996.

5. Cleaner-Burning Gasoline: An Assessment of Its Impact on Ozone Air Quality in California, California Air Resources Board, October 1997.

6. ARB Staff Analysis of Auto/Oil data, Oil Industry data, ARB data, EPA data, and other data, June 1995.

7. Preliminary Assessment of Relative Potential Cancer Risk From California's Reformulated Gasoline, Memo from Joan E. Denton, Ph.D., Manager, Substance Evaluation Section, Air Resources Board to Genevieve A. Shiroma, Chief, Air Quality Measures Branch, California Air Resources Board, November 1995.

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11. An Investigation of Health Concerns Attributed to Reformulated Gasoline Use in Southeastern Wisconsin, Final Report, Wisconsin Department of Health and Social Services, May 1995.

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13. An Assessment of the Health Effects of Reformulated Gasoline in Maine, Task Force on Health Effects of Reformulated Gas, April 1995.

14. Methyl Tertiary Butyl Ether (MTBE): A Review of Exposures and Potential Health Effects, The Connecticut Department of Public Health, January 1996.

15. The Potential Health Effects of Oxygenates Added to Gasoline: A Review of the Current Literature, Health Effects Institute, February 1996.

16. Interagency Assessment of Potential Health Risks Associated with Oxygenated Gasoline, National Science and Technology Council Committee on Environment and Natural Resources, Interagency Oxygenated Fuels Steering Committee, February 1966.

17. Toxicological and Performance Aspects of Oxygenated Motor Vehicle Fuels, National Research Council, June 1996.

18. Preliminary Assessment of the Occurrence and Possible Sources of MTBE in Groundwater in the United States, 1993-1994, P. J. Squillace, J. S. Zogorski, W. G. Wilber, and C. V. Price, Environmental Science and Technology, Vol. 30, No. 5, pp. 1721-1730, 1996.

APPENDIX
List of Internet Addresses with Information on MTBE

California Environmental Protection Agency:
http://www.calepa.cahwnet.gov/epadocs/osmtbefs.txt
MTBE Fact Sheet.

Air Resources Board:
http://www.arb.ca.gov/cbg/pub/pub.htm
Cal/EPA MTBE Briefing Paper; Cleaner-Burning Gasoline publications.

Department of Health Services:
http://www.dhs.ca.gov/org/ps/ddwem/publications/chemicals/mtbe/mtbeindex.htm
Drinking water monitoring data; drinking water standards for MTBE.

State Water Resources Control Board:
http://www.swrcb.ca.gov/~cwphome/ust/usthmpg.htm
Underground Storage Tank Program.

Office of Environmental Health Hazard Assessment:
http://www.calepa.cahwnet.gov/oehha/docs/MTBECALL.htm
Proposition 65 request for MTBE information.

California Energy Commission:
http://www.energy.ca.gov/FR97/
Study of potential impacts of MTBE ban.

United States Geological Survey:
http://wwwsd.cr.usgs.gov/nawqa/vocns/
MTBE bibliography; information on NAWQA urban and agricultural groundwater/land-use studies.

United States Environmental Protection Agency:
http://www.epa.gov/omswww/consumer/fuels/mtbe/mtbe.htm
National Science and Technology Council Report; drinking water advisory; underground storage tank information; fact sheet.

University of California Toxic Substances Research and Teaching Program:
http://www.tsrtp.ucdavis.edu/
Information and updates on the University of California MTBE study required by SB 521.

Association of California Water Agencies:
http://www.acwanet.com/
Water industry concerns, press releases, research, legislative updates.

Oxygenated Fuels Association:
http://www.cleanfuels.net/doc/INNEWS/doc/index4.htm
Oxygenated fuels information; press releases; technical library.