



# Interagency Assessment of Oxygenated Fuels



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*National Science and Technology Council*

*Committee on Environment and Natural Resources*

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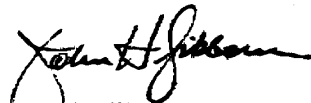
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Dear Colleague:

I am pleased to transmit the *Interagency Assessment of Oxygenated Fuels*, which presents current understanding of critical scientific issues related to the winter oxygenated gasoline program. This program, mandated under the Clean Air Act Amendments of 1990, is implemented in areas that fail to meet the National Ambient Air Quality standard for carbon monoxide. The assessment was done in response to a request from the Environmental Protection Agency for a comprehensive, interagency review of this program for potential health impacts, fuel economy and performance issues, as well as its benefits.

The National Science and Technology Council's (NSTC) Committee on Environment and Natural Resources convened representatives of key Federal agencies and technical experts in government, industry, and academia to participate in this assessment of oxygenated fuels. Draft reports were subjected to extensive peer review, which included evaluation by a panel convened under the auspices of the National Research Council. This final report includes revisions resulting from these reviews.

The *Interagency Assessment of Oxygenated Fuels* provides an authoritative evaluation of existing information and helps to identify areas where the data are too limited to draw conclusions about the impacts of the oxygenated fuels program. Data are insufficient to complete a thorough risk assessment of the oxygenated fuels program; thus several critical issues are currently being researched by several Federal agencies. These agencies are developing plans to expand monitoring and research efforts on occurrence of oxygenates in drinking water, the extent of human exposure to oxygenates, probable effects of human exposures, site remediation, and impacts on aquatic life.



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## **PREFACE**

The use of oxygenated gasoline was mandated under the Clean Air Act Amendments of 1990 in areas that did not meet the Federal ambient air standard for carbon monoxide (CO). Motor vehicle emissions are the primary source of ambient CO levels in most areas and CO is generally seen at its highest levels during the cold weather months. Oxygenated gasoline is designed to increase the combustion efficiency of gasoline, thereby reducing CO emissions.

The Clean Air Act requires at least a 2.7% oxygen content for gasoline sold in CO nonattainment areas, and this level of oxygen is typically achieved by the addition of about 15% methyl tertiary butyl ether (MTBE) or about 7.5% ethanol (by volume). Other fuel oxygenates that are in use to a lesser extent, or that may potentially be used, include ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME), diisopropyl ether (DIPE), and tertiary-butyl alcohol (TBA). Fuel oxygenates, especially MTBE and ethanol, also are used to enhance the octane of conventional gasoline—a practice that started in the late 1970's and continues today.

As a result of the amended Clean Air Act, several new areas were required to begin oxygenated gasoline programs during the winter of 1992-93. Soon after these programs were initiated, anecdotal reports of acute health symptoms were received by health authorities in various areas of the country. Such health concerns were not anticipated but have subsequently focused attention on possible health risks associated with using oxygenated gasoline. These health concerns have been joined by complaints of reduced fuel economy and engine performance, as well as the detection of low levels of MTBE in some samples of ground water.

In order to address public concerns and to take full advantage of the extensive expertise across the Federal Government, as well as outside experts where appropriate, the U.S. Environmental Protection Agency requested the assistance of the Office of Science and Technology Policy (OSTP), through the Committee on Environment and Natural Resources (CENR) of the President's National Science and Technology Council (NSTC), to coordinate a comprehensive assessment of these issues. Working groups that prepared this evaluation were comprised of technical and scientific experts from across several Federal agencies, as well as representatives from State government, industry, and environmental groups.

This assessment is a scientific state-of-understanding report of the fundamental basis and efficacy of the EPA's winter oxygenated gasoline program. The assessment considers air quality, ground water and drinking water quality, fuel economy and engine performance, and the potential health effects of oxygenated gasoline. Each of these subjects is addressed in a separate chapter. Chapter 4 on "Potential Health Effects of Oxygenated Gasoline" is based on two recent reports on health effects—one report was prepared by an Interagency group of health scientists and the second by the Health Effects Institute (HEI) and a panel of experts. Complete citations for these reports are listed in the references for Chapter 4.

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Each chapter in this report underwent extensive external peer-review before submission of the entire report for review by the National Research Council (NRC) of the National Academy of Sciences. Findings and comments from the NRC review have been addressed in this assessment. The entire assessment was reviewed by the National Science and Technology Council.

## EXECUTIVE SUMMARY

### Purpose and Background

Oxygenates have been used as octane enhancers in gasoline since the late 1970s, due to the phaseout of lead. During the 1980s, oxygenates came in to wider use as some States implemented oxygenated gasoline programs for the control of carbon monoxide (CO) pollution in cold weather. People with coronary artery disease are particularly sensitive to the adverse effects of this air pollutant. The first winter oxygenated gasoline program in the United States was implemented in Denver, Colorado in 1988. The 1990 Clean Air Act Amendments required the use of oxygenated gasoline in several areas of the country that failed to attain the National Ambient Air Quality Standard (NAAQS) for CO. During the winter months of 1992-1993, many new oxygenated gasoline programs were implemented to increase combustion efficiency in cold weather and thereby reduce CO emissions.

Methyl tertiary-butyl ether (MTBE) has become the most widely used motor vehicle oxygenate in the U.S., though in some areas, ethanol is the dominant oxygenate used in motor vehicle fuels. Other fuel oxygenates that are in use or may potentially be used include ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME), diisopropyl ether (DIPE), tertiary-butyl alcohol (TBA), and methanol. Because of limitations in available data, there is less emphasis in this report on these other oxygenates. The Clean Air Act requires at least 2.7% by weight oxygen content for gasoline sold in CO nonattainment areas, and about 15% by volume MTBE or about 7.5% by volume ethanol to achieve this requirement.

The purpose of this report is to provide a review of the scientific literature on oxygenated fuels and to assess effects of the winter oxygenated fuels program on air quality, water quality, fuel economy and engine performance, and public health. The request from EPA for this assessment was prompted by public complaints of headaches, nausea, and other acute symptoms attributed to wintertime use of oxygenated fuels, as well as complaints of reductions in fuel economy and engine performance.

This report does not specifically examine the reformulated gasoline program, which is intended to reduce motor vehicle emissions that lead to higher ozone levels during the summer months and air toxics year round, and which also makes use of fuel oxygenates. The report identifies areas where the data are too limited to make definitive conclusions about the costs, benefits, and risks of using oxygenated gasoline in place of conventional gasoline. Several research needs on oxygenated gasoline were identified that would reduce uncertainties and allow a more thorough assessment of human exposure, health risks and benefits, and environmental effects.

### Assessment Findings

#### Air Quality

• A general decline in urban concentrations of CO over the past twenty years is attributed largely to stringent EPA mandated vehicle emission standards and improved vehicle emission control technology. This decline and the effects of meteorology must be accounted for in assessments of air quality benefits of oxygenated gasoline.

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- Analyses of ambient CO measurements in some cities with winter oxygenated gasoline programs find a reduction in ambient CO concentrations of about 10%.
- Studies of the effects of fuel oxygenates on vehicle emissions show a consistent reduction of CO emissions at ambient temperatures above about 50 °F. At temperatures below 50 °F, the magnitude of the reduction is decreased and very uncertain.
- The EPA MOBILE 5a Model appears to overestimate the benefits of oxygenated gasoline on fleet-wide CO emissions by about a factor of two. However, the MOBILE Model is designed for use by the states in preparing highway mobile source emission inventories and estimating the benefits of other air quality programs. This assessment does not address its usefulness for such purposes.
- Oxygenates also reduce total hydrocarbon exhaust emissions. Fuel oxygenates decrease vehicle emissions of the air toxicities, benzene and 1,3-butadiene, but increase the emissions of aldehydes (acetaldehyde from use of ethanol or ETBE and formaldehyde from use of MTBE).
- Older technology vehicles (carbureted and oxidation catalysts) benefit more from the use of oxygenated fuel. The amount of pollutant emissions is smaller in newer technology vehicles (fuel injected and adaptive learning, closed loop three-way catalyst systems). Also, the percentage reductions in CO and hydrocarbon emissions from use of fuel oxygenates are found to be smaller in the newer technology vehicles compared to older technology and higher emitting vehicles.
- Emissions of nitrogen oxides are not changed significantly by low concentrations of fuel oxygenates but some studies indicate increased nitrogen oxide emissions with oxygenate concentrations greater than about 2 % by weight oxygen. The EPA Complex Model developed for the Reformulated Gasoline Program predicts that fuel oxygenate does not increase nitrogen oxide emissions.
- During the winter season, the oxygenates are not removed rapidly from the urban atmosphere, although some scavenging by precipitation is expected. Consequently, the oxygenates are likely to be dispersed and diluted throughout the troposphere, where they ultimately would be removed by slow photooxidation.

### *Water Quality*

- Releases of gasoline containing oxygenates to the subsurface from storage tanks, pipelines, and refueling facilities provide point sources for entry of high concentrations of fuel oxygenates into ground water. In a few instances (such as in Santa Monica, CA) high concentrations of MTBE have caused the shutdown of a drinking-water production well or well field, and the source of contamination was identified as a release from an underground gasoline storage tank. Underground storage tank improvement programs underway by the states and EPA should result in a reduction in the release of gasoline and fuel oxygenates to ground water from these potential point sources.

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- Exhaust emissions from vehicles and evaporative losses from gasoline stations and vehicles are sources of oxygenate release to the atmosphere. Because of their ability to persist in the atmosphere for days to weeks and because they will, in part, partition into water, fuel oxygenates are expected to occur in precipitation in direct proportion to their concentration in air. Hence, fuel oxygenates in the atmosphere provide a non-point, low concentration source to the hydrologic cycle as a result of the dispersive effect of weather patterns and occurrence in precipitation.
  
- Volatilization of the alkyl ether oxygenates will occur slowly from ponds and lakes, and from slow-moving and deep streams and rivers; volatilization can be rapid from shallow and fast-moving streams and rivers. Alkyl ether oxygenates are much less biodegradable than ethanol or the aromatic hydrocarbon constituents of gasoline and, therefore, will persist longer in ground water. They also adsorb only weakly to soil and aquifer material. Consequently, dissolved alkyl ether oxygenates will move with the ground-water flow and migrate further from a point source of contamination.
  
- The current USEPA draft drinking-water lifetime health advisory for MTBE ranges from 20 to 200 µg/L; a revised health advisory is expected. Health advisories have not been developed for other fuel oxygenates.
  
- MTBE was detected in 7% of 592 storm-water samples in 16 cities surveyed between 1991-1995. When detected, concentrations ranged from 0.2 to 8.7 µg/L, with a median of 1.5 µg/L. A seasonal pattern of detections was evident, as most of the detectable concentrations occurred during the winter season. MTBE was detected both in cities using oxygenated gasoline to abate CO nonattainment and in cities using MTBE-oxygenated gasoline for octane enhancement.
  
- At least one detection of MTBE has occurred in ground water in 14 of 33 states surveyed. MTBE was detected in 5% of approximately 1,500 wells sampled, with most detections occurring at low (µg/L-level) concentrations in shallow ground water in urban areas.
  
- Drinking water supplied from ground water has been shown via limited monitoring to be a potential route of human exposure to MTBE. MTBE has been detected in 51 public drinking water systems to date based on limited monitoring in 5 states, however, when detected the concentrations of MTBE were for the most part below the lower limit of the current USEPA health advisory. This indicates that the consumption of drinking water was not a major route of exposure for these few systems. Because of the very limited data set for fuel oxygenates in drinking water, it is not possible to describe for the Nation MTBE's occurrence in drinking water nor to characterize human exposure from consumption of contaminated drinking water.
  
- There is not sufficient data on fuel oxygenates to establish water quality criteria for the protection of aquatic life.



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• The presence of MTBE and other alkyl ether oxygenates in ground water does not prevent the application of conventional (active) methods to clean up gasoline releases; however, the cost of remediation involving MTBE will be higher. Also, the use of intrinsic (passive) bioremediation to clean up gasoline releases containing MTBE may be limited because of the difficulty with which MTBE is biodegraded.

### Fuel Economy and Engine Performance

• Theoretical predictions based on energy content indicate that reductions in fuel economy resulting from the addition of allowable levels of oxygenates to gasoline should be in the range of only 2-3%. On-road measurements agree with these estimates.

• Automobile engine performance problems due solely to the presence of allowable levels of oxygenates in gasoline are not expected because oxygenated gasolines and nonoxygenated gasolines are manufactured to the same specifications of the American Society for Testing and Materials.

### Health Effects

• Complaints of acute health symptoms, such as headaches, nausea, dizziness, and breathing difficulties, were reported in various areas of the country after the introduction of oxygenated gasoline containing MTBE. The limited field investigations conducted to date suggest that greater attention should be given to the potential for increased symptom reporting among workers exposed to high concentrations of oxygenated gasoline containing MTBE. With regard to exposures to lower concentrations as experienced by the general population and motorists, the limited epidemiological studies and controlled exposure studies conducted to date do not support the contention that MTBE as used in the winter oxygenated fuels program is causing significant increases over background in acute symptoms or illnesses. The anecdotal reports of acute health symptoms among some individuals cannot yet be explained or dismissed.

• Human exposure data to MTBE are too limited for a quantitative estimate of the full range and distribution of exposures to MTBE among the general population. Less information is available on exposures to oxygenates other than MTBE.

• The assessment found that chronic non-cancer health effects (neurologic, developmental, or reproductive) would not likely occur at environmental or occupational exposures to MTBE. The observation of acute and reversible neurobehavioral changes in rats exposed to relatively high levels of MTBE is indicative of a neuroactive effect that could hinder performance during periods of high exposure.

• Current data are too limited to quantify health benefits of reduced ambient CO from wintertime use of oxygenated fuels.

• While there are no studies on the carcinogenicity of MTBE in humans, experimental studies indicate that MTBE is carcinogenic in rats and mice at multiple organ sites after inhalation or oral-gavage exposure. The mechanisms by which MTBE causes cancer in animals are not well understood, but are under study. Genotoxicity tests on MTBE and

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one of its metabolites, tertiary-butyl alcohol (TBA), are for the most part negative, whereas the MTBE metabolite formaldehyde is genotoxic in a variety of experimental systems. Formaldehyde is viewed as a “probable” human carcinogen and TBA shows some evidence of carcinogenicity in male rats and female mice. There is sufficient evidence to indicate that MTBE is an animal carcinogen and to regard MTBE as having a human hazard potential. Estimates of cancer potency derived from MTBE animal studies as well as estimates of human exposure to MTBE have large uncertainties and caution is required in their use.

• The estimated upper-bound cancer unit risks for MTBE are similar to or slightly less than those for fully vaporized conventional gasoline; substantially less than that for benzene, a minor constituent of gasoline that is classified as a known human carcinogen; and more than 100 times less than that for 1,3-butadiene, a carcinogenic emission product of incomplete fuel combustion. The interpretation of any health risks associated with the addition of MTBE to gasoline requires a comparison to the health risks associated with the use of conventional gasoline. Meaningful predictions of human cancer risk from the wintertime use of oxygenated gasoline versus nonoxygenated gasoline require much more knowledge of the relative ambient air concentrations and personal exposures to the toxic compounds that are present in both the evaporative and exhaust emissions from both types of fuels.

• It is not likely that the health effects associated with ingestion of moderate to large quantities of ethanol would occur from inhalation of ethanol at ambient levels to which most people may be exposed from use of ethanol as a fuel oxygenate. Potential health effects from exposure to other oxygenates are not known and require investigation if their use in fuels is to become widespread.